Systematic Methodology for Design of Tailor-Made Blended Products: Fuels and Other Blended Products

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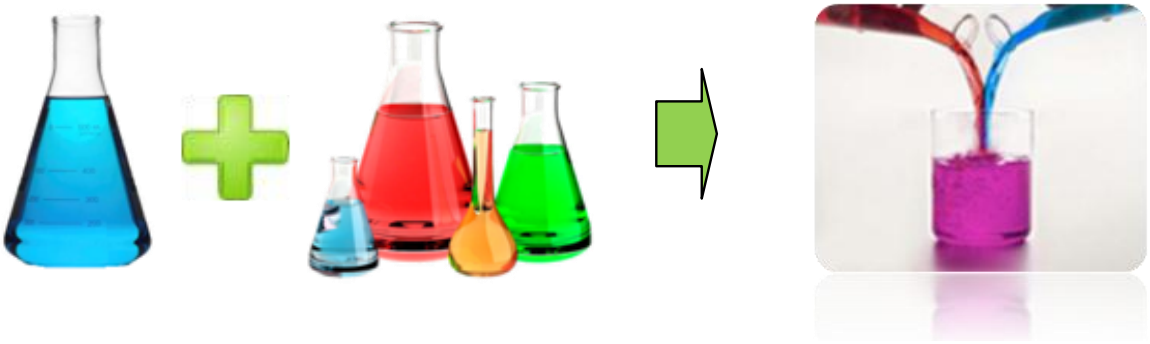

Nor Alafiza Binti Yunus

Ph.D. Thesis

March 2014

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Preface

This thesis is submitted in partial fulfillment of the requirements for obtaining the degree of Doctor of Philosophy (Ph.D.) in Chemical Engineering at the Technical University of Denmark (DTU). This project was done at the Computer Aided Process-Product Engineering Center (CAPEC) of the Department of Chemical and Biochemical Engineering, DTU. This project was carried out from July 2010 until December 2013 under the supervision of Professor Rafiqul Gani, Professor Krist V Gernaey, and Professor John M Woodley.

I am grateful to my supervisors, Professor Rafiqul Gani, Professor Krist V Gernaey, and Professor John M Woodley for their valuable input, guidance and motivation throughout this project. A special thanks to my main supervisor, Professor Rafiqul Gani for his continuous encouragement and support. I would like to thank them for given me the opportunity to work with them in this interesting project.

I would like to thank my committee members: Dr. Ir. Antoon ten Kate (Akzo Nobel, The Netherlands), Dr. Peter Harper (Harper & Vedel, Denmark) and Associate Professor Gürkan Sin (DTU Chemical Engineering) for serving as my committee members even at hardship. I also want to thank you for your brilliant comments and suggestions. Special thanks to Thomas who helped me in translating the thesis abstract into Danish. I would also like to thank all my colleagues in CAPEC for creating a friendly and supportive environment. This includes Amol, Azizul, Deenesh, Fazli, Igor, Katrine, Larissa, Michele, Peam, Sawitree, Thomas and Zainatul.

Finally, I would like to thank my family and friends for being helpful and supportive during my time studying at Technical University of Denmark. Words cannot express how grateful I am to my mother-in law, father-in-law, my father and late mother for all of the sacrifices that you've made on my behalf. Your prayer for me was what sustained me thus far. I am extremely grateful to my husband, Muhammad Imran Ismail for his unconditional love, patience and understanding during the three and half years of my study. To my husband, thank you for always being with me during the hard and easy times.

The work described in this thesis would not have been possible without financial support from the Ministry of Education, Malaysia and Universiti Teknologi Malaysia. I would like to express my gratefulness to them for their contributions towards my scholarships.

Kongens Lyngby, December 2013

Nor Alafiza Yunus

Abstract

A tailor-made blended liquid product is defined as a formulation of various chemicals in the liquid state to obtain a liquid mixture with a specific set of desired characteristics and qualities. Examples of blended liquid products are synthetic fuels and lubricants. This type of products is very important in daily life, since they not only keep people moving around, but also guarantee that machines and equipment work smoothly. The objective of this work is to tackle the blending problems using computer-aided tools for the initial stage of the product design.

A systematic methodology for design of tailor-made blended products has been developed, which has four main tasks. First, the design problem is defined: the product needs are identified, translated into target properties and the bounds for each target property are defined. Secondly, target property models are retrieved from a property model library. Thirdly, a mixture/blend design algorithm is applied to obtain the mixtures/blends that match the design targets. The result is a set of blends that match the constraints, the composition of the chemicals present in the blend, and the values of the target properties. Finally, the mixture target property values are verified by means of rigorous models for the properties and the mixtures. Besides the methodology, as the main contribution, specific supporting tools that were developed to perform each task are also important contributions of this research work.

The applicability of the developed methodology and tools was tested through two case studies. In the first case study, two different gasoline blend problems have been solved. In the second case study, four different lubricant design problems have been solved.

Resume på dansk

Et skræddersyet, flydende blandingsprodukt er defineret som en formulering af forskellige kemikalier i flydende tilstand med det formål at opnå en flydende blanding med et specifikt sæt af ønskede egenskaber og kvaliteter. Eksempler på flydende blandingsprodukter er syntetiske brændstoffer samt smøremidler. Sådanne produkter er meget vigtige i dagligdagen, ikke kun til transport, men også for at sikre at maskiner og udstyr arbejder problemfrit. Formålet med dette arbejde var at løse blandingsproblemer ved hjælp af computer assisteredeværktøjer i den indledende fase af produktdesign.

Der er blevet udviklet en systematisk metode til design af skræddersyede blandingsprodukter, som har fire hovedtrin. I første omgang skal designproblemet defineres: her bliver produktets behov defineret, oversat til ønskede egenskaber, og grænser for de definerede egenskaber bliver opstillet. For det andet bliver egenskabsmodeller for de ønskede egenskaber hentet fra et model bibliotek. For det tredje bliver en blandingsdesign algoritme anvendt til at formulere de blandinger, der matcher designmålet. Resultatet er et sæt af blandinger, hvis egenskaber opfylder de opsatte grænser, selve sammensætningen af de kemikalierne, som indgår i blandingen, og værdierne af de ønskede egenskaber. Endeligt bliver de ønskede egenskaber kontrolleret ved hjælp af detaljerede modeller for egenskaber og blandingerne. Udover hovedbidraget, som består af selve metoden, indgår de målrettede værktøjer, der er blevet udviklet til at udføre hver opgave også som væsentlige bidrag i dette forskningsarbejde.

Anvendeligheden af den udviklede metode og værktøjer blev gennemtestet via to case studies. I det første case study, blev to problemer involverende benzinblandinger løst. I det andet case study, blev fire smøremiddeldesignproblemer løst.

Table of Contents

List of Figures

List of Tables

CHAPTER 1

INTRODUCTION

Over the past decades, chemical product engineering has received much attention among the chemical engineering community. This is due to the transformation of industries in manufacturing and selling chemical products based on the product performance rather than compositional specifications (Hill, 2009). Costa et al. (2006) reported that there is an exponential growth of the number of publications related to chemical product engineering since 1997. Many publications focused on the development of the methodologies and frameworks which are applicable in the product design area, including computer-aided methods (Klein et al., 1992; Gani and Fredenslund, 1993; Constantinou et al., 1996; Moggridge and Cussler, 2000; Wibowo and Ng, 2002) and property modelling and simulation for product design (Gani and Pistikopoulos, 2002). Some authors proposed the product design and engineering as a possible third paradigm in chemical engineering after the first paradigm in 1915 with the introduction of the unit operations concept, and with the transport phenomena as the second paradigm in the late 1950s (Costa et al., 2006; Cussler and Wei, 2003; Hill, 2009). This is due to the fact that solving the chemical product design problem not only requires a chemical engineering approach, but also, more fundamental knowledge (Hill, 2009).

Traditional method used in a new product development is by combining a broad knowledge of existing product with scientific experimentation. The chemical product is developed based on scientific hypothesis, intuition, or simple trial-and-error. Through experimental trial-and-error method, the optimal levels of specified components can be determined and the results are usually quite accurate. Nevertheless, this approach is costly and very time consuming. Since only a limited number of experiments that can be tested at once, the chances to obtain a successful product are very much dependent on luck. For instance, development of a new drug often starts with discovery of new

ingredients and consumes several years of development time and costs millions of dollars. All that effort and money are wasted if the drug does not obtain a marketing license. The high attrition rate of potential drug candidates shows that the latter is a considerable risk in the pharmaceutical industry.

In order to efficiently design chemical products, a systematic methodology is needed. The systematic methodology can be implemented at the intial stage of the design, where it could minimize the required number of experiments systematically, thus increasing the chances of obtaining better solutions with less resources. Several efforts have been reported on the development of systematic methodologies for product design. Ng et al., (2007) proposed an integrated approach that combines a model-based method with experimental work. The model-based steps identifies chemicals and their blended formulations, while the experiments validate the blend properties. At the same time, Cussler and Moggridge (2011) suggested four steps for chemical product design: identify needs, generate ideas, select ideas and manufacture. On the other hand, Churi and Achenie (1997) proposed a mathematical programming approach to design refrigerant mixtures. A small set of individual refrigerants were used as the building blocks in the mixture's design. This approach is practical in obtaining the best mixture by optimizing a performance criterion but the approach only implies one type of ingredient in the mixtures. Besides, Cheng et al. (2009), Conte et al. (2011, 2012) and Teixeira et al. (2012) designed consumer oriented chemicals based products that involve various types of ingredients using different approaches. Cheng et al. (2009) proposed an integrated approach to design a skin care cream, taking into consideration both technical as well as business-related factors. Conte et al. (2011) developed a model-based computer-aided methodology to design and verify formulated products (for example, paint and insect repellent lotion). Conte et al. (2012) added an experimental component to their model-based approach. That is, the final validation, selection and adjustment of the design is made through experiments.

Many techniques and approaches have been proposed to solve specific chemical product designs. Nevertheless, there are still some challenges of this area that need to be overcome. Costa et al. (2006) organized the challenges and opportunities in product design in terms of five generic objectives covering the development of: (1) tools to

convert problem representation spaces from customer needs to technical specifications; (2) modeling and optimization approaches for chemical product design; (3) predictive capabilities for physical properties; (4) systematic approaches supporting chemical product design, and (5) frameworks to effectively link product discovery to R&D efforts.

This work addresses four of the above-mentioned challenges, (1) the knowledge base was developed as a tool for the translation of the product needs to the technical specifications; (2) both model-based and optimization approaches were implemented to solve the blending problems; (3) a group contribution model to predict the heating value was developed; and (4) a systematic approach to design tailor-made blended product using decomposition method was developed.

Design of tailor-made blended products is challenging in different ways. Tailor-made blended products usually have a main ingredient that is mixed with additives, to obtain the desired end-properties. The challenge in the design of these products is to find suitable chemicals and their compositions within the blend such that the end-properties of the resulting product achieve the desired performance. Chemical selection is an important step in blended product design and has the potential to significantly enhance the likelihood of finding truly innovative products. Another challenge is how to deal with the phase behavior issue since by definition, the blended products considered in this work must be stable liquid solutions. Therefore, efficient solution strategies are needed to deal with all the challenges.

The proposed systematic methodology is focusing on the development of a method at the early stage of the product design, which is aimed at generating and selecting promising ideas. The systematic methodology implemented a model-based appraoch by utilizing computer-aided methods that allow the designer to quickly identify the most suitable blend candidates and avoid spending efforts on infeasible regions of the search space. After the candidates are selected, the next stage is to verify the ideas experimentally before they are manufactured in the final stage. This latter part is not considered in this work.

1.1 Motivation

As stated above, this PhD work is focusing on the tailor-made blended products. There are several issues related to tailor-made blended products. An important issue for the production of many chemical-based products is related to the future supply of essential raw materials. Currently, many of these products are derived from fossil fuel based raw materials and from a sustainability point of view other renewable alternatives need to be considered. In order to achieve this, new products need to be developed by blending the conventional materials with other chemicals that can be produced from renewable resources, namely, bio-based chemicals. Blending could offer several advantages, such as reducing the amount of fossil fuel consumption, thus prolonging the fossil fuel supply to some extent. At the same time, the chemical products are safer for humans and for the environment because the harmful chemicals are removed or replaced with safer chemicals as a result of the product design. In addition, the product attributes can also be improved by adding chemicals that have potential to enhance the specific product attribute. The motivation for this project is illustrated through Figure 1.1.

1.2 Project aims and objectives

The objective of this study is to develop a systematic methodology for design of tailor-made blended products using a computer-aided model-based technique. The blending problems deal with single component and multi-component mixtures using various sources of chemicals, mainly crude oils as well as bio-based chemicals.

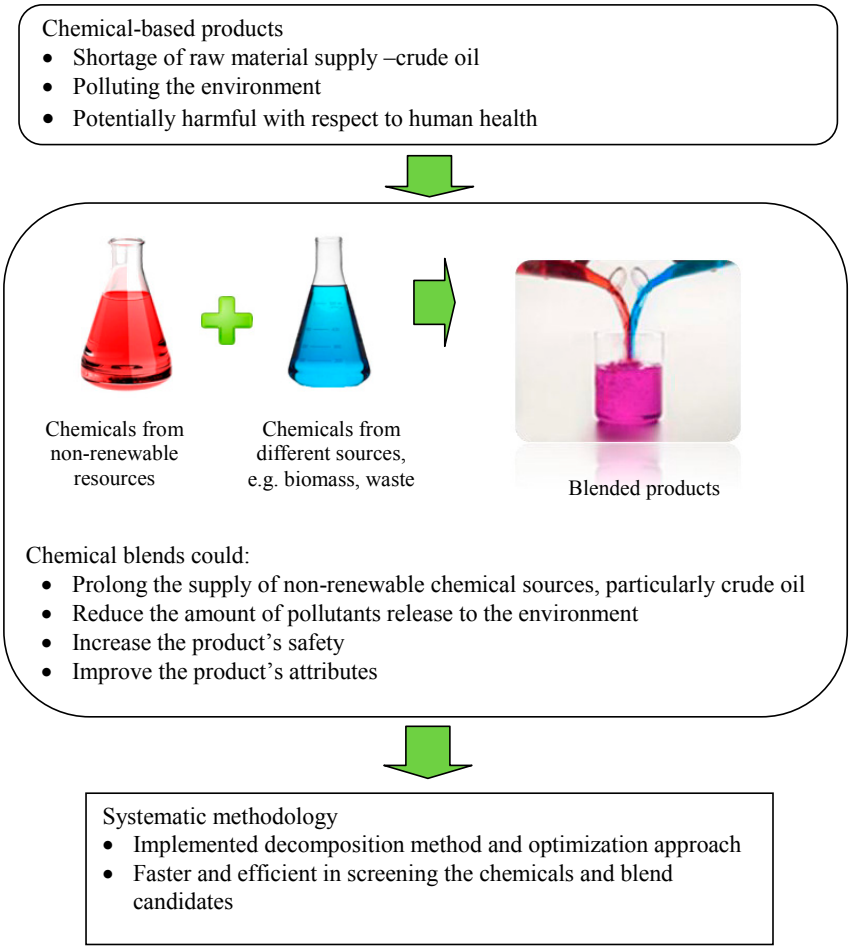

Figure 1.1 Project motivation

1.3 Project scope and significance

In order to achieve the above-mentioned objectives, six main tasks have been identified. They include;

1. Formulation of a general chemical blending problem in mathematical terms.
2. Identification of the necessary property models and development of the unavailable models.

3. Generation and identification of the pure compounds of each design problem, where they are used as building blocks for blends design.
4. Development of a mixture/blend design algorithm as a tool to solve the blending problems.
5. Development of a systematic methodology for tailor-made blended product design.
6. Application of the developed mixture/blend design algorithm on two illustrative case studies.

The scope of the work is defined by the application of the developed methodology, which is applied as initial stage in the product design, where suitable chemicals are selected and blend candidates are proposed for the final stage of product design. At the final stage, the blended products are tested experimentally. Nevertheless, due to time constraints, this final stage is not considered in this work. A model-based approach is employed at the initial stage of product design because it could reduce the search space quickly, by proposing only the promising blend candidates, thus saving time and resources for the experimental work.

The developed method is able to solve chemical blend problems especially dealing with multi-component mixtures. The methodology can be applied to reduce the consumption of raw materials and is especially relevant for problems including a critical raw materials supply, such as fossil fuel for gasoline application. Reduced consumption of scarce raw materials can be achieved by replacing such raw materials with chemicals from other sources such as bio-based chemicals. This method can also be used to design safer and more environmentally friendly products by substituting the harmful chemicals with safer ones. Replacement of the mineral base oils with renewable base oils for lubricant design is an example towards the design of more environmentally friendly products. On the other hand, chemical blending helps to improve the product attributes such as improving the product's quality and can also contribute to reducing the pollutant levels.

The significance of chemical blends can be summarized as follows:

1. Reduce the consumption of critical raw materials such as fossil fuel, so that the life-span of fossil fuel reserves can be extended.

2. Add value to the bio-renewable chemicals by blending them with other chemical products.
3. Reduce the pollutions by replacing the most harmful chemicals with more environmentally friendly chemicals.
4. Increase the safety level of chemical products by substituting the hazardous chemicals with safer chemicals, especially when these chemicals are in contact with humans.

1.4 Thesis summary

This thesis is divided into five chapters. This chapter (chapter 1) introduces the product design and the development of this research area, including the current research state in this area, which forms the motivatetion for this work. The project objectives and scope are explained in this chapter.

Chapter 2 provides the theoretical background on the product design to give a clear explanation of the type of products that are considered in this work. Details about the products, which are gasoline and lubricant, are given in this chapter to provide a better understanding, not only on the product properties, but also the working principle. It is important to understand how this product is working, so that the product behavior can be determined.

Chapter 3 explains the developed methodology in detail, including the tools that are used to perform each task in the methodology. The property model library, the chemical database and the mixture/blend design algorithms that are developed in this work are presented in this chapter.

Chapter 4 presents the blend design case studies that have been solved, which are focused on gasoline and lubricant blends. A total of six different problems within this two case studies were solved in this chapter to highlight the application of the developed methods and tools.

Chapter 5 concludes the work that has been done, it summarizes the achievements and includes recommendations for future work.

CHAPTER 2

BACKGROUND INFORMATION

This chapter provides a literature review of product design in the section 2.1 followed by information on the type of blended products that are considered in this work. Section 2.2 focuses on gasoline, while section 2.3 focuses on the fundamentals of lubricants.

2.1 Literature review

Cussler and Moggridge (2011) identified four categories of chemical products, while Costa et al. (2006) classified chemical products into five categories. Combining both ideas, the product classification can be summarized as follows,

- Commodities: They are produced in large quantities using feedstock most often from petroleum and natural gas. They are sold on the basis of their purity.
- Specialty chemicals: Pure compounds that are produced in small quantity as opposed to commodities, and sold based on their specific benefit or function. An example of specialty chemical is surfactant.
- Formulated products: They are defined as the combined systems consist of several components and are often multifunctional. They are designed to meet end-used requirements. A good example of these products is cosmetics and food consumer goods.
- Devices: They carried out a physical or chemical transformation at a small scale, for example, electrolytic device used to convert salt into chlorinated pool disinfectant.

As previously mentioned in Section 1.1, this PhD project is concerned with the tailor-made blended (liquid) products, which are also classified as formulated products. Tailor-made blended liquid product is defined as a formulation of various chemicals in the liquid state having a set of desired characteristics and qualities. Examples of blended liquid products are synthetic fuels and lubricants. Consumer-oriented liquid product is one of the formulated products, which are also blends of chemicals, where a solid active ingredient is dissolved and blended with other chemicals. For example, the formulation of an insect repellent contains a solid active ingredient that is responsible for the main function of the product, solvents that deliver the active ingredient, and additives that enhance the quality of the product (Conte et al., 2011). The blended liquid products, on the other hand, contain one or more liquid chemicals that serve as the main ingredient and perform the main function of the product (for example, release heat when combusted or absorb heat or release and take up heat in a cyclic operation) and additives that enhance the quality of the product. For example, a lubricant blend may contain a specific base oil as the main ingredient and a set of additives. The base oil primarily determines the lubricant performance and the additives enhance its quality. In this work, only the class of formulations that are blended liquid mixtures are considered, and they will be referred to as tailor-made blended products throughout this article.

Two design problems are considered in this work, which are gasoline and lubricant blends. Designing this type of products requires understanding of the product functionality as well as technical fundamental. Next two sections describe the product specifications and working principle of the gasoline and lubricant.

2.2 Gasoline

Gasoline is produced from the fractionation of crude oil. A typical gasoline consists of numerous hydrocarbons with four to 12 carbon atoms per molecules (C4 - C12). The gasoline is predominantly composed of four chemicals types, which are paraffins (alkanes), nafthenes (cycloalkanes), olefins (alkenes) and aromatics. The composition varies according to the location of refineries, crude oil feeds and the gasoline grades. Gasoline may also contain small levels of contaminants, which are mainly sulphur compounds such as hydrogen sulfide and thiol. They must be removed because they

cause corrosion in engines. They also contain small amounts of other organic compounds and additives. Table 2.1 lists the typical properties of a gasoline and diesel fuel.

Table 2.1 Gasoline and diesel fuel properties **(**http://www.methanol.org)

Property	**Gasoline**	**Diesel Fuel**
Chemical Formula	C4 to C12	C3 to C25
Molecular Weight	100–105	≈200
Composition, Weight %		
Carbon	85–88	84–87
Hydrogen	12–15	33–16
Oxygen	0	0
Specific gravity, 15.5° C/15.5° C	0.72–0.78	0.81–0.89
Density, g/cm^3 @ 15.5° C	0.72–0.78	0.81–0.89
Boiling temperature, °C	26.6–225	187.7–343.3
Reid vapor pressure, kPa	55–103	1.4
Research octane no.	90–100	-
Motor octane no.	81–90	-
Cetane no.	5–20	40–55
Viscosity , Centipoise @ 15.5° C	0.37–0.44	2.6–4.1
Flash point, closed cup, °C	-42.7	73.8
Autoignition temperature, °C	257.2	≈315.5
Latent heat of vaporization, kJ/kg @15.5° C	≈349	≈233
Heating value		
Higher (liquid fuel-liquid water) MJ/kg	43.7–47.5	44.7–46.5
Lower (liquid fuel-water vapor) MJ/kg	41.9–44.2	41.9–44.2
Mixture in vapor state, MJ/cubic meter @ 20° C	3.55	3.61
Specific heat, kJ/kg °C	1.12	1.00
Stoichiometric air/fuel, weight	14.7	14.7
Volume % fuel in vaporized stoichiometric mixture	2	–

In general, gasoline can be categorized into two types, conventional and reformulated gasoline (RFG). Conventional gasoline is regular gasoline produced from crude oil refinery. This type is the most popular and widely available in most regions.

Reformulated gasoline also known as cleaner fuel is regulated to reduce their environment impact. In United States, RFG is required to be used in metropolitan areas where air pollutions are high. RFG is different from conventional gasoline but should give similar performance. It has lower amount of compounds that contribute to air pollution such as aromatics, benzene and olefins. It also may contain chemical oxygen (oxygenates) to enhance the octane number. RFG has lower volatility and do not evaporate easily during summer. The characteristics of both types of gasoline are given in Table 2.2.

Table 2.2 Characteristic of gasoline

	Conventional	**Reformulated gasoline**
Definition	Regular gasoline	Regular gasoline that has been modified in terms of properties and/or composition to suit with locations or temperature.
Composition	Varies depending on the crude oil sources	Contain low levels of certain compounds that contribute to air pollution, such as benzene, olefins and aromatics. May contain oxygenates.

Both types have their advantages and disadvantages as listed in Table 2.3. Reformulated gasoline have lower energy content than conventional gasoline as they contain oxygenates. For instance, a car running for 11 km per liter with conventional gasoline may get 10.89 km per liter for reformulated gasoline. The reduction is about 1% of energy content of reformulated gasoline. However, this is only a minor factors that affects the gas mileage. Driving habits, traffic congestion, weather conditions, and vehicle maintenance are among factors that affect the mileage to a greater extent.

Table 2.3 Advantages and disadvantages of both types of gasoline

	Conventional gasoline	**Reformulated gasoline**
Vehicle performance	Generally better vehicle performance	A little changes on the vehicle performance
Oxygenates content	Have low oxygen and typically no oxygen	Have higher oxygen content
Property	High volatility	Lower volatility
Emission	Emit significant amounts of harmful emission	Emit less harmful emissions

2.2.1 Principle of combustion process in spark-ignition engine

Figure 2.1 shows complete ignition process from step i to v of a spark ignition engine. The ignition process is starting from injection of an amount of fuel into a close tank by spraying them into droplets. The fuel droplets are vaporizing and mix with air. Then, the ignition source is igniting to initiate the combustion in engine. The combustion produces an amount of heat of combustion, which is converted to kinetic energy to power vehicle or any moving parts, while the exhaust emissions produced are released to the atmosphere. Figure 2.1 illustrates the flow of fuel in the engine and Figure 2.2 shows the role of fuel properties in each step of the ignition process.

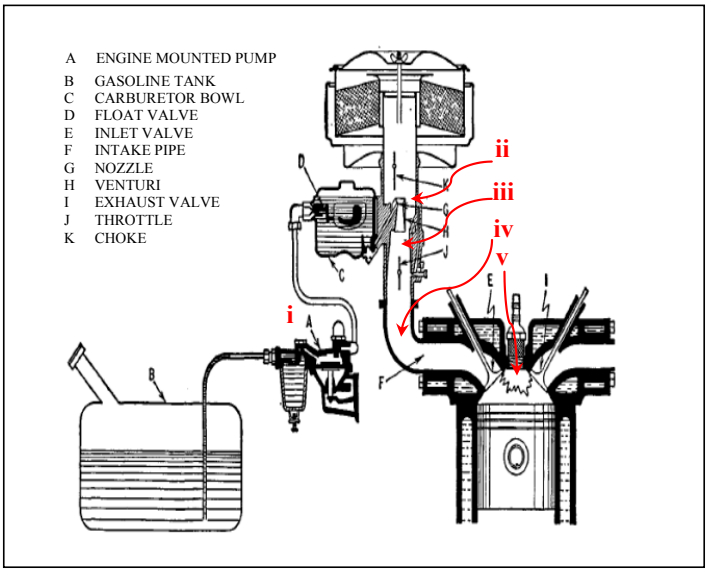

Figure 2.1 Spark ignition process in gasoline engine and related fuel properties (Guthrie, 1960)

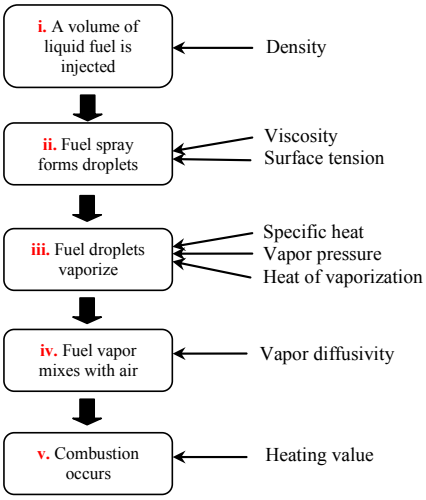

Figure 2.2 Steps of the ignition process combustion

2.2.2 Requirements of good gasoline blends

What are the requirements of good gasoline? Gasoline must meet the specifications, which varies according to the region, altitudes and temperatures in order to give high engine performance. Gasoline must evaporate easily and burn completely. It also must be chemically stable and no particulate contaminants or entrained by water. There are several requirements to have a good gasoline:

i. Physical properties:
   - *Octane*. Octane rating is the most important gasoline properties and widely used to measure the gasoline quality. Using low octane gasoline might cause engine knocking. Knock is caused by pre-ignition or unwanted chemical reactions in the combustion chamber, resulting in loud noise in the engine. Long exposure to knock may cause engine damage.
   - *Volatility*. There are two properties related to gasoline volatility, Reid vapor pressure (RVP) and distillation temperature. These properties are very important in order to control the gasoline evaporation rate. Too much volatility can cause engine startability problems. The volatility of gasoline should be increased at reduced temperatures.
   - *Heating value.* The capability of a fuel is determined by the heat content.
   - *Density.* This property determines the amount of fuel needed and it is affected the fuel price.
   - *Viscosity*. This property used to measure the resistance of flow and ensure the fuel flowing continuously.
   - *Flash point*. This property is important in order to ensure that the fuel burn only at a certain temperature.

From the above mentioned gasoline attributes, the gasoline needs can be identified as listed in Table 2.4. Each target property has its significance on the gasoline behavior.

Table 2.4 Target properties and their significances on the gasoline attributes

Target property	Significance
i. Good fuel performance	
Octane number	ON used to measure of the knock resistance of gasoline where combustion-knock can cause engine damage. Higher ON helps to run vehicle smoothly and keep the vehicle's fuel system clean for optimal performance.
Heating value	The power of fuel is determine by heat content of the compounds.
Vapor pressure	Volatility is a very important property because fuel won't burn until they vaporize. A lower RVP makes a cold-start ignition problem at a low ambient temperature, while higher RVP cause startability problems due to vapor lock.
Kinematic Viscosity	This property is used to measure the resistance to flow in order to ensure that fuel flow continuously.
Water content	Water should not be presented in gasoline. Higher water content in gasoline blend causes phase separation and consequently, damages the engine.
Density	This property determines the amount of fuel needed
ii. Environmental	
CO and NO_x emissions	These greenhouse gases' emissions must be reduced.
Oxygen content	Oxygen is required to reduce the amount of toxic aromatics in gasoline and also reduce GHG emission. It also could enhance the octane number.
iii. Safety	
Flash point	This property used to determine the flammability limit of a fuel.

ii. Chemical factors: Chemical types play an important role in determining the fuel properties, engine performance as well as emissions control. Chemical structure is one of the factors affecting the knock process. Longer paraffin chains and saturated aromatic rings could increase the knock tendency, while isomerising normal paraffins and alkylating aromatics reducing knocking tendency. Therefore,

selection of suitable chemicals is one of the important criteria needs to be considered before design of gasoline blends. Some of the chemicals not only affect the gasoline performance and/or attributes but are also incompatible with engine parts. The type of chemicals is, however, still considered in gasoline design. Types of chemicals are listed in Table 2.5 with their advantages and disadvantages.

Table 2.5 Advantages and disadvantages of chemicals as gasoline additives

Chemical types	Advantages	Disadvantages
Olefins /diolefins	• Higher ON than corresponding paraffins	• High sensitivity • Poor stability and oxidize to form gums during storage
Alcohol	• Reduce carbon monoxide emissions • Octane booster	
Ether	• Octane number enhancer • Miscible with gasoline without azeotrope formation • Low vapor pressure	
Amines & Amides	• Rust inhibitor • Corrosion inhibitor	
Aromatic	• High octane number(Guthrie, 1960)	
Carbonyl group (Ketone, aldehyde, ester)		• Not compatible with some engine parts, elastomeric seals and diaphragms
Carboxylic acid		• Corrosive to metal
Cycloalkanes		• Mostly compound have low to medium octane number
Nitrogen		• Degrade the gasoline stability
Benzene		• Carcinogen • Release toxic emissions (Hochhauser, 2007)
Water		• Caused phase separation in mixture

iii. Cleanliness: Gasoline must be chemically and physically clean. Chemically clean means the gasoline must not react during storage and form by-products such as gums, sludge and deposits, while physically clean means no undissolved solids such as small particles, and large amount of water in gasoline.

iv. Other requirements
- Gasoline should not promote rust in pipeline, station tanks, or vehicle parts. Additives can be added to gasoline to achieve this specific purpose.
- Sulfur should be avoided in gasoline due to corrosive characteristic and it could damage the sensitivity of a catalytic converter.
- Gasoline should not contain free water or pick up any water from ambient.
- Gasoline should not contain more than trace amount of carbonyls which can dissolve elastomeric seals and diaphragms.

2.3 Lubricant

Lubricants are required in almost all modern machines. Lubricating oil is a substance introduced between two moving surfaces to reduce the friction between them, improving efficiency, and reducing wear. The function however, depends on the applications. Five main functions of a lubricant are identified as follows:

1. Lubrication (reduce friction and wear) – the main function of a lubricant is to reduce friction and wear between two moving parts.
2. Cooling (heat transfer) – lubricant absorbs heat and removed away from the critical moving parts
3. Cleaning and suspending – lubricant removes and suspends the harmful product such as deposits, carbon, soot, sludge and other materials such as dirt and debris. This function is important for operations that involve high operating temperature.
4. Protection - lubricant prevents metal damage due to corrosion, oxidation, and wear.
5. Transfer power – lubricant is used as medium for transferring power from power source to the parts that perform the actual work.

Typically lubricants are a mixture of base oil and performance package, and a viscosity modifier is added for multi-grade oils. The ratio of these components in the lubricant varies according to application. Figure 2.3 highlights the approximate ranges of each component in the lubricant. The most important component in a lubricant is the base oil, which comprises 65 – 98 percent of the total composition of the lubricant. The performance additives are added to achieve the required performance degree and end-user requirements. For instance, additives added to reduce friction, increase resistance to corrosion and oxidation and to avoid contamination. Viscosity modifier is required to adjust the viscosity and viscosity index of multi-grade lubricants. The largest component is base oil, thus it primarily determined the properties of lubricants.

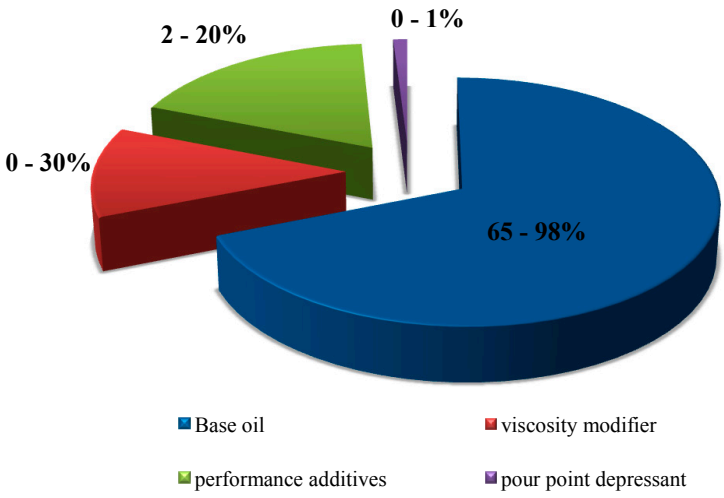

Figure 2.3 Typical lubricant composition (Rizvi, 2009)

i. Base oil – it is the largest component in lubricant, which determines the properties of the lubricant. Three types of most commonly used base oil: mineral, synthetic and vegetable oils.

ii. Additives – added to achieve required performance and end-user requirements, for instance, reducing friction and wear, increasing oxidation and corrosion resistance, and removing impurities.

iii. Viscosity modifier – this required for multi-grade oils.

Base oil is derived from three sources: petroleum, synthetic and biological, i.e. originating from plants or animals. The vegetable oils are the first generation lubricants, uses dates back to 1650 B.C. Since petroleum was discovered in late 1800s, the mineral oils have dominated the lubricant markets replacing vegetable base oil. It is due to their lower price and better overall performance. Later on, the synthetic oil was developed as a way to deal with shortage of crude oil products, making it possible to use natural oil more efficiently. Synthetic oils are good alternatives of lubricants due to their superior properties compared to those of mineral oil lubricants. This type of lubricants can perform well in extreme conditions either in cold or hot climates and also have long life spans. The synthetic oils have excellent physical and chemical properties. Nevertheless, the synthetic oil might not be the best option when lubricant cost, toxicity, solubility and environmental issue need to be considered.

Mineral oils derived from petroleum are the most widely used base oils. Mineral oil contains a mixture of many hydrocarbons, which comprises different percentages of paraffins, naphthenes and aromatics. Mineral oils with a high content of paraffins are suitable for high-temperature applications because they have high melting point. Nevertheless, aromatics and unsaturated chemicals are unfavoured due to excessive lubricant oxidation. Table 2.6 listed several mineral base oils with their properties and compositions.

Meanwhile, synthetic oils are man-made oils with superior properties, thereby performing well in extreme conditions. The synthetic oils have homogeneous molecular structure because they are synthesized using identical straight chained structures. The difference in molecular structure of lubricants is illustrated in Figure 2.4. Synthetic oils have a constant molecular size and weight while they vary greatly for mineral oil. On the other hand, vegetable oils are easily degraded, but have poor properties, making them suitable only for low demand applications. Comparing various types of base oils, it can be concluded that synthetic oils have excellent physical and chemical properties, but they are expensive, while mineral oils are cheaper but less environmentally friendly, and vegetable oils are biodegradable but have poor oxidative stability and cold flow properties. The comparison is summarized in Table 2.7.

Table 2.6 Different type of petroleum based oil and their properties

Property	Naphthenic (A)	Naphthenic (B)	Hydro-cracked (C)	Hydro-cracked (D)	Commercial oil (E)	Commercial oil (F)
Viscosity, cSt at 40°C	7.5	29.8	42.0	39.5	16.79	19.79
Viscosity, cSt at100°C	2.07	4.55	6.3	6.7	3.789	4.119
Specific gravity at 15°C	0.877	0.910	0.865	0.8343	0.8348	0.8478
Viscosity Index	56	35	95	125	116	109
Cloud point, °C	-	-	-	-	-16	-20
Pour point, °C	-54	-39	-15	-18	-21	-23
Molecular weight, g/mol	-	-	-	-	386.2	354.5
Hydrocarbon type analysis						
C_P,%	42	-	-	-	-	-
C_N,%	52	-	-	-	-	-
C_A,%	6	-	-	-	-	-
Weight percent,%						
Paraffinics (P)	-	-	-	-	20.6	14.58
Naphthenes (N)	-	-	-	-	79.13	85.42
Aromatics (A)	-	-	-	-	0.27	0

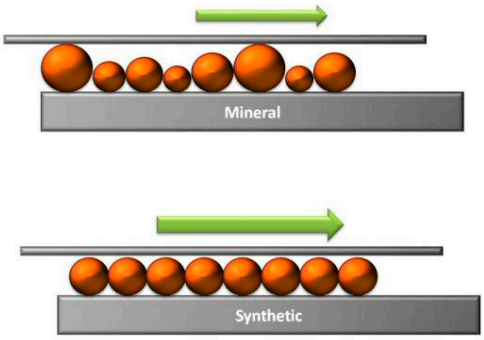

Figure 2.4 Different molecular distributions of mineral and synthetic lubricants

Table 2.7 Comparison of lubricant base oils

Criteria	Vegetable oil	Mineral oil	Synthetic oil
Source	Plant (palm oil)	Crude oil	Man-made
Lubrication properties	Poor	Inferior	Superior
Cost	Cheap	Cheap	Expensive

2.3.1 Application of lubricant

The application of lubricant is classified into two types, engine lubricants and non-engine lubricants. Engine lubricants are used to lubricate components of an internal engine, such as gasoline and diesel engine. Non-engine lubricants are used to lubricate parts and mechanisms that help transfer power from power source to the parts that perform the actual work. The working environment for these two types of lubricants is different. Engine lubricants perform in an open atmosphere, where it is highly oxidative and exposed to the combustion process in an internal engine. Meanwhile, non-engine lubricants perform in a closed space, thus less oxidative in nature. In this work, the lubricant is designed as engine oils, which is the largest application of lubricants. Engine oils accounts approximately 57% of lubricants used in the world, and 28% is used in passenger cars, for example, the gasoline engine. Different end uses of lubricants are shown in Table 2.8.

Table 2.8 Lubricant classification (Rizvi, 2009)

Engine oils	**Non-engine lubricants**
Gasoline engine oils	Transmission fluids
Diesel engine oils i. Automotive diesel oils ii. Stationary diesel oils iii. Marine diesel oils	i. Automatic transmission fluids ii. Manual transmission fluids iii. Power transmission fluids
Stationary gas engine oils	Gear oils i. Automatic gear oils ii. Industrial gear oils
Aviation engine oils	Hydraulic fluids i. Tractor hydraulic fluids ii. Industrial hydraulic fluids
Two-stroke cycle engine oils	Turbine oils
	Miscellaneous industrial oils
	Metalworking fluids
	Greases

2.3.2 Working principle of lubricant

Figure 2.5 illustrates the lubrication system for gasoline engines. Oil is pumped from the sump and passed through a filter before being delivered to a system of passages or channels drilled through the engine. Oil is sprayed on the cylinder walls, cams and up into pistons to lubricate the piston pins. Excess oils drip into the oil pan, where they are collected and recycled to the lubrication system. The recycle oil must be filtered to remove the solid contaminants that are collected from the engine parts.

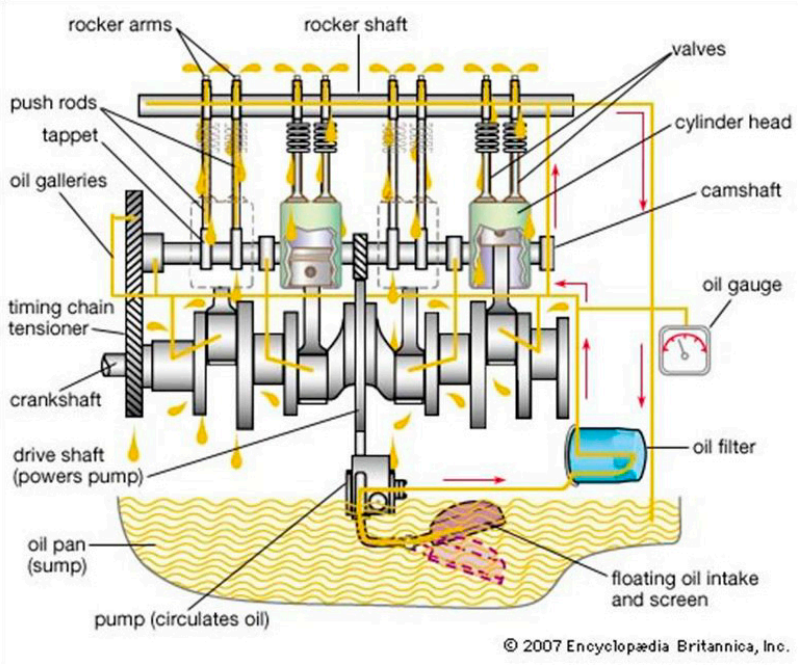

Figure 2.5 Typical gasoline engine lubrication system (www. global.britannica.com)

2.3.3 Properties of lubricant

Basic performances of a lubricant are able to reduce friction between two moving surfaces and able to suspend and remove the impurities. Furthermore, engine oils must have the following criteria:

1. Do not oxidize easily and retain in high temperature operation
2. Able to maintain proper viscosity to form a stable oil film at certain temperature
3. Able to remove heat from combustion chamber
4. Prevent corrosion and must be neutral

These lubricant functions need to be considered when designing the lubricant blends. Besides, other factors such as environmental issues and safety aspects also need to be taking into consideration. These needs are translates into target properties as given in Table 2.9.

Table 2.9 Target properties of lubricant and their significance

Need	Property	Description
Able to lubricate and prevent wear	Viscosity	It measures the resistance to flow. Higher viscosity produces high resistance and powerful lubricity attributes. Base oil forming a thin layer on the moving surface that could prevent wear. Viscosity is the key property of base stock because it is used for base oil grading. Base oils are manufactured and sold according to the base stocks viscosities.
Able to operate at a high temperature	Viscosity index	It measures the extent of viscosity change with temperature.
Able to flow at the surrounding temperature	Cloud point Pour point	It measures the temperature at which a base oil start forming the microcrystal and no longer flow.
Handling purpose	Density and gravity	Handling quantities of the base stocks.
Safety	Flash point	It measures the temperature at which there is sufficient vapor above a liquid to ignite. It is to prevent fire occurs in the lubrication system.
Environmental	Volatility	It measures losses to ambient by evaporation. Low volatility produce minimal losses at high temperature, therefore reduce emissions and oil consumption.

2.4 How blends changes the product attributes and performance

Mixing or blending of two or more different chemicals is possible to achieve matching various targeted properties of the chemical-based products. Three examples of the blended products are given to give an overall overview of the blend behaviors.

i. *Gasoline blend*: Gasohol is a well-known example of gasoline blending, which has been commercialized in many countries such as Brazil, Canada, United States and Thailand. Gasohol is a mixture of gasoline with ethanol, typically at 10 percent of ethanol and 90 percent of gasoline. In 10 liter of gasohol usage, 1

liter of gasoline can be saved. Therefore, the reduction of gasoline consumption can increase the reserve crude oil supplies to some extent. Furthermore, adding ethanol in gasoline can reduce the amount of harmful exhaust emissions. Study by Al-Hassan (2003) and Najafi et al. (2009) found that carbon monoxide (CO) and unburned hydrocarbon emission are decreased with gasoline blends fuel. On the other hand, the amount of harmful chemicals, such as benzene can be reduced by adding ethanol. Benzene is a carcinogenic chemical that has negative health effects and also may contaminate the ground water in case of leakage. All the advantages mentioned above can be achieved regardless of the product's attributes. Adding ethanol enhances the octane number, which reduce knocking tendency. Nevertheless, the gasohol performance is slightly affected due to lower energy content of ethanol. The binary mixture of gasoline reduces the consumption of crude oil, but needs more fuels to have similar performance as the conventional gasoline. In order to maintain/improve or improve the performance of the fuel, it is necessary to have the best gasoline blend with the most appropriate bio-based chemicals.

ii. *Lubricant blend*: A lubricant consists of base oil and additives. Base oil of a lubricant can be mineral oil, vegetable oil or synthetic oil. The base oils can be mixed. For example, semi-synthetic lubricant is a mixture of mineral oil and synthetic oil. The mixture may contain synthetic oil up to 30%. The blending can replace an amount of mineral oil with synthetic oil or other chemicals derived from renewable sources, thus the mineral oil consumption can be saved. From an environmental point of view, the main problem of lubricants is the disposal of used lubricants in a proper way because it may contain harmful chemicals. Lubricant blends can be formulated to have the biodegradable chemicals and low toxicity chemicals as the ingredients in lubricant formulation. Other than making the lubricants are more compatible with the environment, they are also safe for human.

iii. *Refrigerant blend*: R-407C is a zeotropic mixture of difluoromethane (R-32), pentafluoroethane (R-125) and 1,1,1,2-tetrafluoroethane (R-134a) as a substitute for chlorodiflouromethane (R-22). It has been used in low temperature refrigeration systems such as cold storage application. R-407C is a hydrofluorocarbon (HFC) refrigerant with zero ozone depletion potential (ODP) and 1700 of global warming potential (GWP), that means R-407C will trap 1700 times more heat than the carbon dioxide over next 100 years. ODP and GWP are two properties used to measure the environmental effects of a refrigerant. ODP is measured between ranges of zero to one, and GWP is calculated over specific time, commonly, 20, 100 and 500 years. Compared to R-22, the ODP is reduced from 0.05 (R-22) to zero, while GWP is about 6 percent reduction. Therefore, the harmful substances released to the atmosphere are reduced. Furthermore, R-407C is designed to have similar performance as R-22, so that the product qualities as a refrigerant are fulfilled. Nevertheless, higher volumetric of R-407C is needed in order to achieve the same performance as R-22. Therefore, refrigerants that have almost zero ODP and GWP, and can perform well in the refrigeration system with only a small amount of refrigerants are needed

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CHAPTER 3

METHODS AND TOOLS

In this chapter, the development of methods and tools used to design tailor-made blended products are presented. The first section in this chapter, Section 3.1 gives an overview of the general blending problem formulation, followed by the work-flow of the methodology in Section 3.2. The development of tools and method used to solve design problems of blended products is then explained in Section 3.3. This includes: i) the development of the property models library; ii) the development of the chemical database that contains the chemicals and their associated properties required for the design of blended products; iii) the mixture/blend design algorithm that is used to generate and screen the mixture/blend candidates.

3.1 General problem formulation

The general problem for tailor-made chemical blends is formulated as a Mixed Integer Non-Linear Programming (MINLP) problem. The product performance index is optimized subject to product attributes (target properties), process specifications and/ or cost. The design objective is limited by the mixture constraints, product property constraints and process model constraints. The mixture constraints model is represented by Eq. (3.2). Any factors that prohibit the formulation of mixtures/blends are called mixture constraint. An example of the mixture constraints is the miscibility/solubility property that indicates the phase behavior of the mixtures/ blends. The miscibility is very important in liquid blending because it determines the feasibility of the mixtures/ blends. Eq. (3.3) is property constraint model to represent the target properties defined from the product needs. The product property constraint is unique for each product design problem. The process model constraint, Eq. (3.4), denotes the conditions for the blending or mixing process, for example, mass and energy balance. A restriction on the design

parameters is also considered as process model constraint, for instance, the limitation of the composition in blends.

Considering multiple types of constraint equations, a general tailor-made liquid chemical blend problem is formulated as:

$$min \ or \ max \ f_{obj}(X, Y, Q, E, S) \tag{3.1}$$

Subject to:

$$\text{Mixture constraints: } g_1(X, Y) > 0 \tag{3.2}$$

$$\text{Product property constraints: } \zeta_{LB} \leq g_2(X, Y, \zeta) \leq \zeta_{UB} \tag{3.3}$$

$$\text{Process model constraints: } g_3(X, Y) = 0 \tag{3.4}$$

where f_{obj} is the objective function to minimize/maximize one or more of the following parameters: the blend composition (x), the type of mixture (y), cost (C), environmental impact (E), safety factor (S) or product performance (Q); y is an integer variable, which is related to the type of mixtures; x is a continuous variable, which is related to the mixture compositions; while ζ corresponds to a vector of target properties; subscripts *UB* and *LB* represent the upper and lower limits, respectively; g_1 is the mixture's constraints with respect to the blend miscibility and solubility condition that must be satisfied; g_2 is a vector of target property constraints translated from product needs, for example, viscosity; g_3 is a vector of other constraints such as the definition of mole or weight or volume fraction.

The above blending problem involving a large database of chemicals and non-linear constraints creates a combinatorial explosion within a very large search space. By employing a systematic decomposition based solution approach (Karunanithi et al., 2005), it is possible to manage the complexities of the blend design problem efficiently and to reduce the search space. The decomposition based solution approach divides the MINLP problem into several sub-problems that are relatively simple and easy to solve.

3.2 General overview of the work flow

Figure 3.1 illustrates the design steps employed in tailor-made chemical blend design. The systematic methodology for solving mixture/blend design problems consists of four main tasks: 1) problem definition 2) property models identification 3) mixture/blend design, and 4) model-based verification. Additional tools and methods are developed to perform a specific task in the methodology, which are, the property model library (§3.3), the chemicals database (§3.4), and the mixture/blend design algorithm (§3.5).

3.2.1 Task 1 Problem definition

Task 1.1 Identify product needs. The needs for blended products are primarily determined from the principal product function, which is the main reason for the products to be sold. For example, for an engine lubricant, the principal function is to reduce the resistance and prevent wear between two moving surfaces. A blended product may have more than one principal function. Besides, requirements from environmental regulation and safety are also considered as additional constraints in the design of these blended products. A knowledge base, literature search and legislation details are used to determine the product needs in this work.

Task 1.2 Translate needs into physico-chemical properties. A specially developed knowledge base is used to transform the product needs into target properties. Note that not all the product needs can be evaluated using a model-based approach, such as color, odor and shelf life. However, when validated models are available, it is easier and faster to test on the basis of models rather than performing experiments.

Task 1.3 Set the target values. The target values are retrieved from the knowledge base for similar products. The target values may also be changed for improvement of the product's performance or criteria.

3.2.2 Task 2 Property model identification

Task 2.1 Retrieve the required property models from the library. The necessary property models and their parameters are obtained from the model library. It contains property models for mixture and pure component properties that defines the blend design problem (see Tables 3.2 – 3.3). Different blend problems need a different set of property models.

3.2.3 Task 3 Mixture/blend design

Task 3.1 Collect input data. The input data for this task are the main ingredient properties and composition, and a list of chemicals with their associated properties.

Task 3.2 Generation and screening. Generate and screen for all feasible blend alternatives using the mixture/blend design algorithm. Further explanation of this algorithm is given in Section 3.3.1. Other tools employed in this task are, a STABILITY tool for miscibility test, and a chemicals database, for the list of chemicals that are to be considered in the blend design.

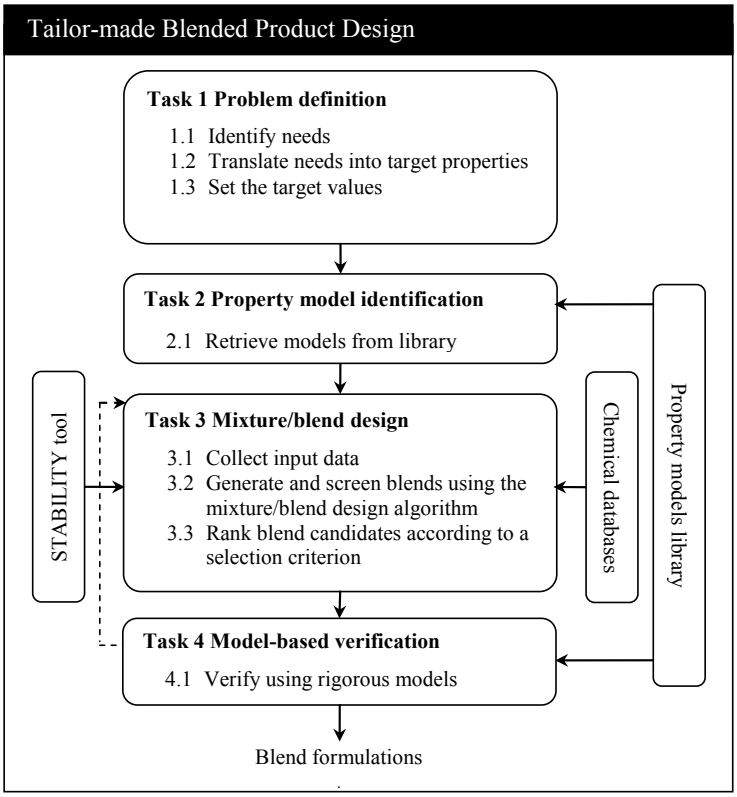

Figure 3.1 Work flow of the systematic methodology for design of tailor-made blended product

Task 3.3 Rank blend candidates. Rank the results of the mixture/blend design algorithm according to a selected criterion. The selection criterion can be blend composition, any target property, performance criterion or cost, if available.

Tools employed in this task are the STABILITY tool for miscibility test, and chemical database, which provides a list of chemicals used as building blocks in the blend design.

3.2.4 Task 4 Model-based verification

Task 4.1 Verification. Here, the objective is to verify the mixture property values by means of rigorous models for the properties and mixtures that require it. For example, a linear mixing rule is used to estimate the viscosity of blends. The model gives a good prediction for ideal mixtures. However, the linear models may have significant errors for non-ideal mixtures. Therefore, further verification using rigorous models is necessary.

Finally, verify the mixture property values by means of rigorous models for the properties and mixtures that require it. First, identify properties that are estimated using linear mixing rules. Then, examine the type of chemical system (mixtures) according to these three type of fluids; normal fluid (NF), for example, alkane and benzene; Polar Non-Associate (PNA) such as ester and ether; and Polar Associate (PAS) such as alcohol, water, acid carboxylic. The chemical system is categorized into two types as follows:

1. A mixture of two similar fluids; NF/NF and PNA/PNA (except PAS/PAS)
2. Any other kind of mixture; NF/PNA, NF/PAS, PNA/PAS and PAS/PAS.

For mixture type one, this step is unnecessary because the linear mixing rules give a reliable estimation for this type of mixture. If the mixtures are type two, then the properties need to be verified using rigorous models. If the new target values are within the range, the final blend formulations are obtained. Otherwise, repeat Task 3 for the corresponding blends by giving the new composition as input and find new blend formulations.

If the target values are not matched with the rigorous property models, then Task 3 is repeated for the corresponding blends by assigning new compositions as input until a matching blend formulation is found.

The result from this task is a set of blends that satisfy all property targets and that can now be further verified, if necessary. Table 3.1 lists the methods and tools required in the methodology.

Table 3.1 List of methods and tools used in the blend design methodology

Tasks	Description	Methods /Tools
Task 1.1	Define needs	Knowledge base
Task 1.2	Translate needs into target properties	Knowledge base
Task 1.3	Set the target values	Knowledge base
Task 2.1	Retrieve property models	Property models library
Task 3.1	Collect input data	Chemical database
Task 3.2	Generate and screen blends using the mixture/blend design algorithm	Mixture/blend design algorithm, STABILITY tool
Task 3.3	Rank blend candidates according to a selection criterion	Selection criteria
Task 4.1	Verify the properties of blend candidates	Property models library, Experimental data

Three tools were developed specifically for this work in order to solve the blending problem. They are; the mixture/blend design algorithm for generating the blend candidates and screening them systematically; the chemicals database to store chemicals to be used as building blocks in blend design; and the property models library to store the property models that are required in the design. In addition, a STABILITY tool developed by Conte et al. (2011) was employed to identify the miscible blends.

3.3 The property model library

The property model library was created to store all the property models needed for design of blended products. A list of the target properties to design gasoline and lubricant blends is given in Table 3.2. The last column shows the function of the respective models that requires pure component properties. The pure component properties are either obtained from the experimental data if they are available or estimated using the models given in Table 3.3.

The property model library is divided into two sections; pure component property models, used to estimate the pure component properties needed for the mixture property models; and the mixture property models, used to estimate the target properties of the blended products. This section also comprises rigorous models, used for verification purposes.

Table 3.2 Target property models, and their function

Target property	**Model**	**Function**
Dynamic viscosity, η	linear mixing rule	$f(\eta_i, x_i)$
	GC(UNIFAC)-based method (Cao et al., 1993)	$f(\eta_i, \gamma_i, x_i)$
Kinematic viscosity, ν	Definition, $\nu = \frac{\eta}{\rho}$	$f(\eta, \rho)$
Viscosity Index , *VI*	Correlation (Rizvi, 2009)	$f(\nu)$
Higher Heating Value, *HHV*	linear mixing rules	$f(HHV_i, x_i)$
Density, ρ	linear mixing rule (on the molar volume basis)	$f(\rho_i, x_i)$
	Modified Rackett equation (Spencer and Danner 1973)	$f(T, x_i)$
Research Octane number, *RON*	linear mixing rules	$f(RON_i, x_i)$
Reid Vapor Pressure, *RVP*	GC(UNIFAC)-based method	$f(P_i^{sat}, \gamma_i, x_i)$
Oxygen content, Wt_{O2}	linear mixing rules	$f(Wt_{o2,i}, x_i)$
Open cup flash point, T_f	GC(UNIFAC)-based method (Liaw et al., 2002; Liaw et al., 2004)	$f(T_{f,i}, \gamma_i, x_i)$
Cost, *C*	linear mixing rules	$f(C_i, x_i)$
Toxicity parameter, LC_{50}	linear mixing rules	$f(-logLC_{50,i}, x_i)$
Energy of mixing, ΔG^{mix}	UNIFAC (Magnussen et al., 1981)	$f(GC, segments, x_i)$
Pour point, *PP*	linear mixing rules (on the blending index) (Fahim et al., 2010)	$f(PP_i, x_i)$

GC: group contribution (structure of the compound)

Table 3.3 Pure component property models

Pure component property	Model	Function
Higher heating value, HHV_i	GC method (developed)	$f(GC)$
Density, ρ_i and dynamic viscosity, η_i	Correlation (Nielsen et al., 2001)	$f(T)$
Kinematic viscosity, ν_i	Definition	$f(\eta_i, \rho_i)$
Vapor pressure, P_i^{sat}	Correlation (Nielsen et al., 2001; Yaws, 2003)	$f(T)$
Open cup flash point, $T_{f,i}$	C&G GC method (Constantinou and Gani 1994)	$f(GC)$
Melting point, T_m	M&G GC based method	$f(GC)$
Cost, C_i	Correlation	$f(\rho_i)$
Lethal concentration, $LC_{50,i}$	M&G GC based method (Hukkerikar et al., 2012a)	$f(GC)$

3.3.1 Pure component property models

The pure component property models are necessary in order to estimate the missing properties of a compound. A compound with an unknown property will be removed. It could possibly be one of the potential candidates in the blended product. Hence, property models play a very important role in the blended product design, which could highlight the qualities of a compound.

3.3.1.1 Higher heating value (HHV)

The potential power of a fuel is measured from its heating value. The heating value is defined as the amount of heat released during complete combustion of a unit of fuel (Luis et al., 2012). It is also called heat of combustion, gross calorific value or total heating value. Heat of combustion is measured at standard temperature and pressure (25^{o}C and 101.33kPa) including heat of vaporization of water. Although experimental data for heat of combustion can be found in literature, there is still an essential need of this data in chemical product design. A predictive model is necessary for estimation of the missing properties of a compound or unknown compound.

A group contribution method is a commonly used method for estimation of the pure component properties because it is simple and not computationally demanding. This approach is applied for prediction of pure component properties, such as, melting point, boiling point, enthalpy of vaporization, flash point, as well as environment-related

properties (Marero and Gani, 2001; Hurikkerikar et al., 2012). The GC method has been proven to be able to provide a good prediction and only requires chemical structure as input. Due to its predictive capability, the GC method was considered for estimation of the heat of combustion.

The GC method of Marrero and Gani (2001) was implemented, where the group contributions were determine through a three-step regression procedure. The first step was considered only for simple and monofunctional compounds; the second step includes polyfunctional, aromatic and aliphatic compounds; and the third step involves large, complex and polycyclic compounds. Eq. (3.5) represents the general form of the function, *f(X)* of the target property *X*.

$$f(X) = \sum_{i}^{NG1} N_i C_i + w \sum_{j}^{NG2} M_j D_j + z \sum_{k}^{NG3} O_k E_k \tag{3.5}$$

where C_i is the contribution for the first-order group of type-i with N_i occurrences; D_j is the contribution for the second-order group of type-j with M_j and E_k is the contribution of the third-order group of type-k with O_k occurrences; and w and z are the constants for the second-order and third-order groups, respectively.

Several tasks were performed in order to develop the GC method to estimate the higher heating value property as follows:

- Collect the experimental data
- Choose a suitable property function, F(*HHV*)
- Regress the group contributions using the collected experimental data.

Data collection: A data set of heat of combustion (at 298K and atmospheric pressure) was collected from an open database (Linstrom and Mallard, 2011), which contains 532 compounds from the common families, such as alcohol, ether, ester, acid, aromatic as well as polyfunctional compounds. The data points are given in Appendix A.

Property function selection: Selection of the appropriate property model function is an important step in the GC method. The property function was selected based on the data trend of the higher heating value. It must show the best possible fit of the experimental

data and should also provide a good extrapolation capability. The collected experimental data of heat of combustion was plotted versus occurrences of the CH_2 group for various families of compounds. Figure 3.2 shows that the heat of combustion increases linearly with the CH_2 group suggesting that the appropriate form of the property function is the linear function. Hence, the heat of combustion model is represented by Eq. (3.6).

$$H_c = H_{co} + \sum_{i}^{NG1} N_i H_{c1i} + w \sum_{j}^{NG2} M_j H_{c2j} + z \sum_{k}^{NG3} O_k H_{c3k} \tag{3.6}$$

where H_c is heat of combustion, and H_{co} is a universal constant.

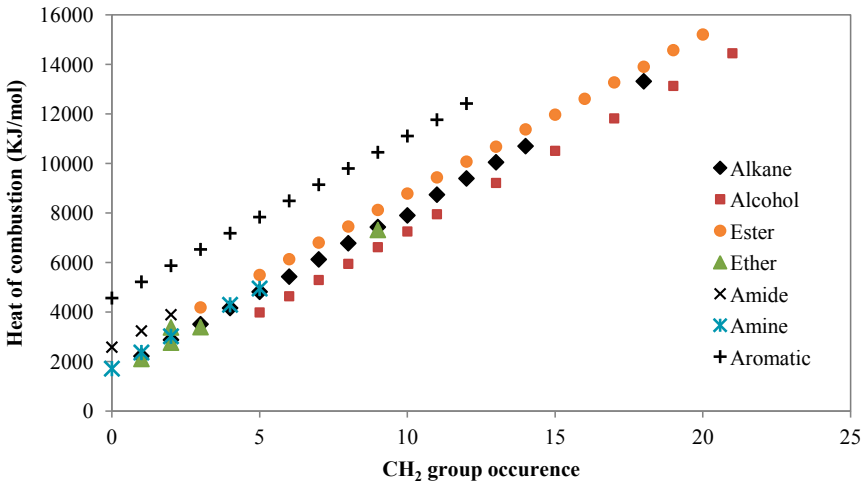

Figure 3.2 Heat of combustion versus the occurrence of the CH_2 group for different families of compounds

Parameter regression: The parameter regression of the contribution, C_i, D_j, and E_k was carried out in three steps. The first step is to determine the contribution of the first-order groups, C_i and also the universal constant, H_{co} where w and z constants were assigned zero values. Then, w was set to unity, z was set to zero and D_j was determined by regression using the contribution of the first-order groups, C_i and H_{Co} obtained in the previous step. Finally, both w and z values were set to unity, and the contributions of the third-order groups, E_k, were determined. The results of the regression were analyzed to identify the outliers in the experimental data. The outliers are the outcome of inaccurate

experimental measurements, for example, due bad instrument calibration. If the obtained values have high error and did not fit in the average trend, these values may disturb the parameter regression, which could result in an erroneous parameter estimation. The identified outliers were removed, and the GC model parameters were regressed again all at once using the obtained parameters, C_i, D_j, and E_k as initial values. The overall work-flow for the parameter regression is shown in Figure 3.3.

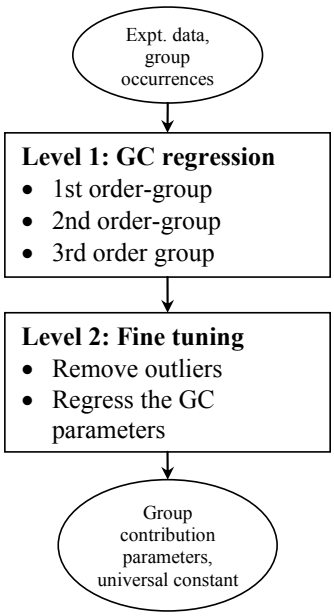

Figure 3.3 The work-flow of the parameter regression

The results of the first-level regression has identified four data points that are outliers, i.e. they do not follow the average trend. These data were removed, and the parameters were regressed again to obtain better GC model contributions. The estimated value of heat of combustion was well fitted with the experimental data (see Figure 3.4). The group contributions are given in Appendix B. The statistical analysis of the Standard Deviation (SD), the Relative Deviation (RD), the Average Absolute Error (AAE) and the Average Relative Error are defined by Eq. (3.7) – (3.10).

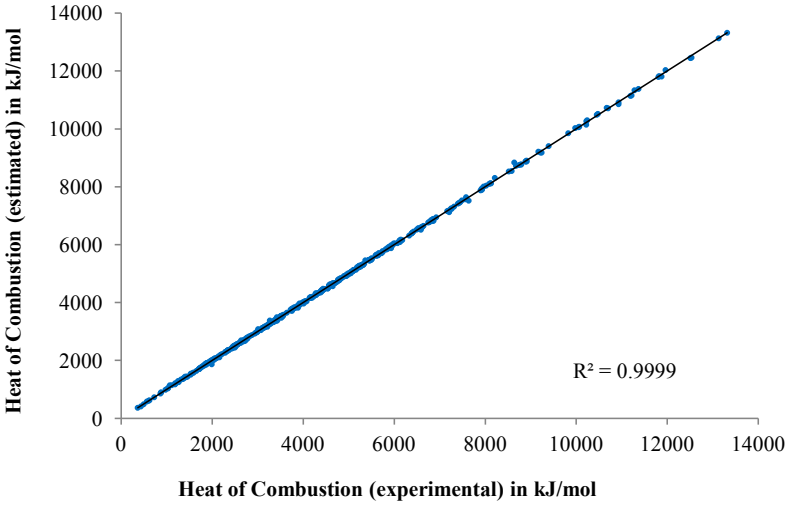

Figure 3.4 Predicted versus experimental data of heat of combustion

$$SD = \sqrt{\frac{\sum_i (\zeta_i^{pred} - \zeta_i^{exp})^2}{N}} \qquad i = 1,2 \dots 301 \qquad (3.7)$$

$$RD = \frac{\left|\zeta_i^{pred} - \zeta_i^{exp}\right|}{\zeta_i^{exp}} \cdot 100 \qquad i = 1,2 \dots 301 \qquad (3.8)$$

$$AAE = \frac{\sum_i \left|\zeta_i^{pred} - \zeta_i^{exp}\right|}{N} \qquad i = 1,2 \dots 301 \qquad (3.9)$$

$$ARE = \frac{\sum_i RD_i}{N} \qquad i = 1,2 \dots 301 \qquad (3.10)$$

where N is the number of data point, ζ_i^{pred} and ζ_i^{exp} are the predicted and experimental value of heat of combustion, respectively. The statistical analysis results are given in Table 3.4, where a very good prediction quality is demonstrated with the R^2 value close to unity.

Table 3.4 Statistical results from the regression of the heat of combustion

Statistic analysis	Value
R^2	0.9999
Average absolute error, AAE	17.83
Average relative error, ARE	0.4855
Standard deviation, SD	26.96

In order to prove the capability of the model, it was tested with a set of extra data points (51 compounds) that were collected separately. The result of that prediction is illustrated in Figure 3.5. The model shows a good prediction with an R^2 value of 0.9985. The experimental data and estimated values for 51 compounds are reported in Appendix C. Five of the data points are highlighted in Table 3.5.

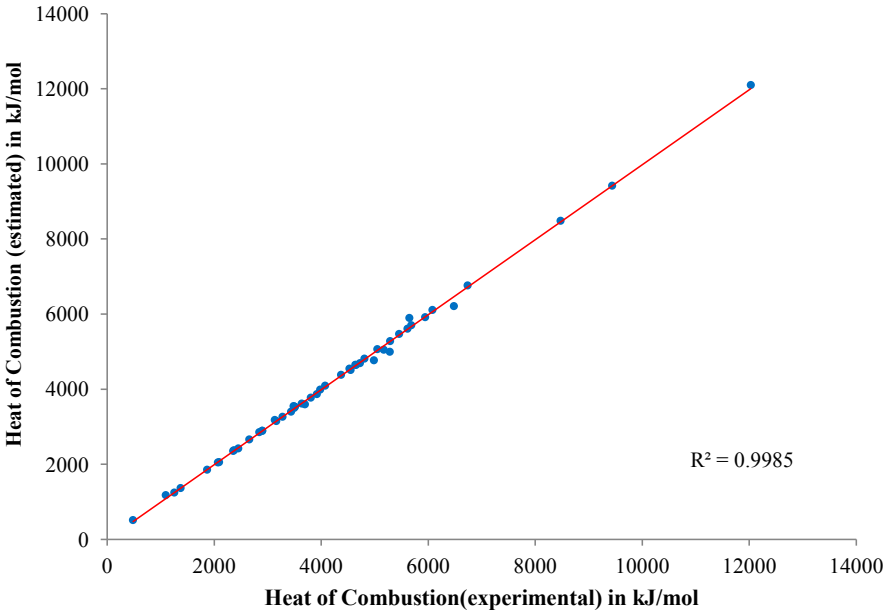

Figure 3.5 Predicted versus experimental data of heat of combustion of the extra data points (51 compounds)

Table 3.5 Comparison of the estimated and experimental heat of combustion, and the RD

Compound	CAS nr	*-Hc exp* (kJ/mol)	*-Hc est* (kJ/mol)	*RD%*
Pentane	109-66-0	3509	3526	0.49
1-Hexanol	111-27-3	3981	3988	0.18
Acetylacetone	123-54-6	2655	2661	0.22
Acetic acid, ethoxy-, ethyl ester	817-95-8	3437	3400	1.06
Acetamide, ethoxy	51770-98-0	2369	2373	0.13

3.3.1.2 Liquid density, liquid viscosity and vapor pressure

Liquid density (ρ), liquid viscosity (η) and vapor pressure (P_i^{sat}) are the temperature-dependent properties. These properties were estimated using regression models, where their coefficients were obtained from the CAPEC database (Nielsen et al., 2001) and Yaws (2003).

The liquid density, ρ_i (kmol/m^3) was estimated using Eq. (3.11), where T is temperature in Kelvin (K). Meanwhile, the correlation to estimate the liquid viscosity and vapor pressure is represented by Eq. (3.12), where ζ_i is either P_i^{sat} (Pa) or η (kg/m.s), and T is temperature in Kelvin (K).

$$\rho_i = A_i / B_i^{[1+(1-T/C_i)]^{D_i}} \tag{3.11}$$

$$\ln \zeta_i = A_i + B_i/T + C_i lnT + D_i T + ET^2 \tag{3.12}$$

3.3.1.3 Flash point, melting point, and lethal concentration

Flash point (T_f), melting point (T_m) and lethal concentration ($-logLC_{50}$) were estimated using the group contribution method (Marrero and Gani, 2001). For the compound that is not completely described by any available groups, the group-contribution$^+$ (GC$^+$) model, a combination of group-contribution (GC) method and atom connectivity index (CI) method was applied (Hukkerikar et al., 2012a; Hukkerikar et al., 2012b). These prediction methods were implemented in the ProPred software (Hukkerikar, 2013), where the molecular structure of the pure component was used as input to predict their

properties, such as, critical temperature, flash point, melting point, lethal concentration, solubility parameter, etc.

3.3.2 Mixture property models

The mixture property models are applied in product design to estimate the product's performance. The models used in this work are collected from a literature survey. The details of each model are explained in this section.

3.3.2.1 Linear mixing rule

The simplest mixture property model is the linear mixing rule, which corresponds linearly to the properties of the pure compounds. The linear mixing rule for target properties, ζ is represented by Eq. (3.13).

$$\zeta = \sum_{i=1}^{n} x_i \zeta_i \tag{3.13}$$

where ζ_i is the property of component *i*; x_i is the mass, volume or molar fraction of component *i;* and *n* is the number of compounds in mixture. This model gives a good prediction for mixtures that have negligible excess properties of mixing, also called ideal mixtures. For non-ideal mixtures, the estimated properties need to be verified using rigorous models since their excess properties of mixing need to be considered.

The target properties of the blended product that were determined using the linear mixing rule are density (molar volume basis), heating value, oxygen content, viscosity and octane number.

3.3.2.2 Vapor pressure and flash point

Vapor pressure is defined as the pressure exerted by a vapor of the solid or liquid phase with which it is in equilibrium. The vapor pressure for blended gasoline is referred as the Reid vapor pressure (*RVP*), which is defined as the vapor pressure measured at a temperature of 100^{o}F (308 K) in a chamber with a vapor/liquid volume ratio of 4:1 (Andersen et al., 2010). The *RVP* model is derived from the modified Raoult's law, a function of the composition, activity coefficient and saturated vapor pressure as presented in Eq. (3.14). The activity coefficient, γ_i is a function of temperature and

composition. In this work, the UNIFAC method was used to estimate the activity coefficients (Smith et al., 2005).

$$RVP = \sum_{i=1}^{n} x_i \gamma_i P_i^{sat} \tag{3.14}$$

Flash point (T_f) is defined as the lowest temperature at which the vapor above a liquid can be ignited in air. The flash point of a mixture was determined using Eq. (3.15), which is adopted from the work by Liaw et al. (2011) and Liaw and Li (2010).

$$\sum_{i=1}^{n} \frac{x_i \gamma_i P_i^{sat}(T)}{P_{i,T_f}^{sat}} - 1 = 0 \tag{3.15}$$

where P_i^{sat} is the saturated vapor pressure at temperature T; γ_i is the activity coefficient; and P_{i,T_f}^{sat} is the vapor pressure of pure components at their flash point. The temperature, T is deemed to be the flash point of the mixture. This property model requires an iteration to obtain the flash point of the mixture, thus it is only used for those mixtures that have been shortlisted.

3.3.2.3 Pour point

The pour point (*PP*) is defined as the lowest temperature at which, a substance or a mixture is still capable of flowing or be poured under specified conditions. The pour point is not an additive property. In order to have a linear mixture model, pour point blending indices were used, so that the mixture can be blended linearly on a volume basis as represented by Eq. (3.16). Meanwhile, the pour point blending indices, BI_{PP} were estimated using Eq. (3.17). These models were retrieved from Fahim et al., (2010).

$$BI_B = \sum_{i=1}^{n} x_{vi} BI_{PPi} \tag{3.16}$$

$$BI_{PPi} = PP_i^{1/0.08} \tag{3.17}$$

where BI_B is the blending index of the mixture, x_{vi} is the volume fraction of component i in the mixture, BI_{PPi} is the pour point index of component i, and PP_i is the pour point of component i, in K. The measurement for a pure compound corresponding to the pour point of a compound is the melting point, which in practice is the temperature at which

the liquid and crystalline phases are in equilibrium. The pour point of the blend, PP_{Blend} was evaluated by the reversed form of Eq. (3.13).

3.3.2.4 Viscosity Index

The viscosity index (VI) is the most common method used to determine the viscosity-temperature characteristics of a fluid. The VI is an arbitrary scale from 0 to 100, where high VI indicates that the fluids have low sensitivity to temperature. Oils with high VI are generally preferred for use in most lubricants. The VI of oil was determined using the relationship in Eq. (3.18) by comparing its kinematic viscosity with the viscosity of 0 and 100 VI oils, at 40°C. The 0 and 100 VI are the reference oils that must have the same kinematic viscosity as the oil of interest at 100°C (Rizvi, 2009).

$$VI = \frac{L - U}{L - H} \times 100 \tag{3.18}$$

where, L is the viscosity of 0 VI oil, U is the viscosity of the blended oil, and H is the viscosity of 100 VI oil. All the viscosities were measured at 40°C. Note that the viscosity in the *VI* model refers to the kinematic viscosity, in cSt.

Nevertheless, the *VI* model has some limitations, where it is only applicable for viscosity values greater than 2.0 cSt. Zakarian (2012) compared several methods to predict the viscosity-temperature characteristic and found that the proportional *VI* (*PVI*) is a more realistic viscosity-temperature rating method. In addition, *PVI* method can be used also to estimate the viscosity index for low viscosity oil using the correlation given in Eq. (3.19).

$$PVI = \frac{\alpha \cdot \nu(100)^{\beta}}{\nu(40)} \times 100 \tag{3.19}$$

$\nu(100)$ is the kinematic viscosity of the 100 *VI* oil at 100°C and $\nu(40)$ is mixture/blend viscosity at 40°C, respectively. The α and β values are given as 2.611 and 1.4959, respectively.

The *VI* model was applied to estimate the viscosity-temperature properties for the lubricant blends because it has been widely used in rating the lubricant grade. Nevertheless, the *PVI* correlation was used if t he *VI* model is not applicable.

3.3.2.5 Vapor loss

Volatility of the lubricant prsent in the lubricated system can contribute greatly to the loss of lubrication efficiency. When losses are larger, it may lead to equipment failures, and, in addition, the vapors may cause environmental pollution. The amount of lubricant loss, therefore, is restricted to a certain limit according to the standard regulation for each specific application. In order to estimate the vapor loss, the state of the lubricant blends is first determined at the specified temperature by calculating the bubble point (P_{bubl}) and dew point (P_{dew}). If the pressure in the system, P lies between P_{bubl} and P_{dew}, this indicates that the system is in two phases, and the amount of vapor loss, V is evaluated using Eqs. (3.20) – (3.23). Otherwise, the blend exists as one phase, either totally liquid or vapor. If the mixture is liquid, the vapor loss is considered as zero, and total loss for vapor state.

$$\sum_{i=1}^{n} \frac{z_i K_i}{1 + V(K_i - 1)} = 1 \tag{3.20}$$

$$K_i = {P_i}^{sat}/P \tag{3.21}$$

where z_i is the mole fraction of the mixture, and K is the equilibrium ratio. The bubble point calculation is represented by Eq. (3.22) with z_i=x_i and Eq. (3.23) is used to calculate the dew point with z_i=y_i, where x_i and y_i are the mole fraction of liquid and vapor, respectively.

$$P_{bubl} = \sum_{i=1}^{n} x_i {P_i}^{sat} \tag{3.22}$$

$$P_{dew} = 1 \Big/ \sum_{i=1}^{n} (y_i / {P_i}^{sat}) \tag{3.23}$$

3.3.2.6 Dynamic viscosity

The rigorous viscosity model was obtained from Cao et al. (1993). The model can be represented by Eqs. (3.24) – (3.31) below.

$$ln(\eta V) = \sum_{i}^{NC} \varphi_i ln(\eta_i V_i) + 2 \sum_{i}^{NC} \varphi_i ln\left(\frac{x_i}{\varphi_i}\right) - \sum_{i}^{NC} \left(\frac{q_i np_i \varphi_i}{r_i}\right) \sum_{j}^{NC} \theta_{ji} ln(\tau_{ji}) \tag{3.24}$$

where η(mPa.s) is the mixture viscosity; V (cm^3/mol) is the mixture volume that can be calculated by Eq. (3.25). V_i (cm^3/mol) and η_i (mPa.s) are pure compound molar volume and viscosity as follows:

$$V = \sum_{i}^{NC} x_i V_i \tag{3.25}$$

Parameters, r_i and q_i are calculated using Eq. (3.26) and (3.27) respectively.

$$r_i = \sum_{i}^{NC} \upsilon_{k,i} R_k \tag{3.26}$$

$$q_i = \sum_{i}^{NC} \upsilon_{k,i} Q_k \tag{3.27}$$

$\upsilon_{k,i}$, R_k and Q_k are group parameters obtained from Magnussen et al., (1981); τ_{ij} is calculated from the group interaction parameters a_{mn}.

$$\tau_{ij} = exp\left(-\frac{a_{mn}}{T}\right) \tag{3.28}$$

The volume fraction, φ_i and parameter θ_{ji} are calculated using Eqs. (3.29) - (3.30), respectively. Meanwhile, the surface fraction, θ_j is calculated using Eq. (3.31) .

$$\varphi_i = \frac{x_i r_i}{\sum_j^{NC} x_j r_j} \tag{3.29}$$

$$\theta_{ji} = \frac{\theta_j \tau_{ji}}{\sum_l^{NC} \theta_l \tau_{li}} \tag{3.30}$$

$$\theta_j = \frac{x_j q_j}{\sum_i^{NC} x_i q_i} \tag{3.31}$$

3.3.2.7 Density

The modified Rackett equation gives the best prediction of the pure component density for hydrocarbons, and provides a good estimation for organic as well as inorganic compounds. Therefore, the modified Rackett equation was extended for estimation of the mixture's density, ρ_B (Spence and Danner, 1973).

$$\frac{1}{\rho_B} = V_{Cm} Z_{RAm}^{[1+(1-T_r)^{\frac{2}{7}}]} \tag{3.32}$$

where V_{cm} and Z_{RAm} are molar averages of the pure component critical volumes and critical compressibility factors, estimated using Eqs. (3.33) – (3.34), respectively.

$$V_{Cm} = \mathrm{R} \sum_{\mathrm{i}=1}^{\mathrm{n}} x_i \frac{T_{ci}}{P_{ci}} \tag{3.33}$$

$$Z_{RAm} = \sum_{\mathrm{i}=1}^{\mathrm{n}} x_i Z_{RAi} \tag{3.34}$$

$$T_r = \frac{T}{\sum x_i T_{ci}} \tag{3.35}$$

where Z_{RAi} is the particular constant for the Rackett equation for compound *i*. However, it can be replaced by the critical compressibility factor, Z_c if it is not available. Meanwhile, the reduced temperature is calculated using the average pure component critical temperatures by using Eq. (3.35). The unit of measurement for mixture density is mol/cm^3, depending on the universal gas constant, *R*.

3.4 The chemicals database

The chemicals database was created to store the compounds, used as the ingredients in blended product design, and their physico-chemical properties. The ingredients were divided into two types, which are main ingredients (*MI*) and additives. The compounds and properties of the main ingredients were collected from a literature survey. Meanwhile, the database for additives contains the chemicals that are commonly found in a particular blended product and various chemicals, that are generated using the computer-aided molecular design (CAMD) technique (Harper et al., 1999). The additives database also includes the physico-chemical properties, which are divided into non-temperature dependent and temperature-dependent properties. These properties were retrieved from the CAPEC database (Nielsen et al., 2001) and handbooks (Brandrup et al., 1999; Yaws, 2003). The missing pure component properties, for instance, flash point, lethal concentration, solubility, etc., were predicted using the property prediction tool

(Hukkerikar et al., 2012b). Note, that experimental data were always used if they were available.

In order to give a flexibility of chemical choices in the design of blended products, a large additives database is needed. To fill the gaps in the additives database, more chemicals are generated using CAMD, a computer-aided tool used to synthesize the molecular structures using the group contribution approach. By defining the types of compounds to be generated and constrained by a set of pure component properties, it can generate thousands of structures. The structures were identified either in the CAPEC database or in open databases. Meanwhile, their physico-chemical properties and the associated parameters for temperature-dependent properties were retrieved from the CAPEC database, and handbooks. The missing pure properties were estimated using ProPred. The work-flow of the database generation is illustrated in Figure 3.6.

3.4.1 Database development work-flow

The database is generated using three simple steps; problem definition, structures generation and structures selection. It is developed based on the design problems solved in this thesis. The database is divided into two sections, which is gasoline and lubricant.

- *Step 1: Problem definition*

  Define needs: The chemicals database needs were carefully defined according to the design problems that were to be solved, in order to have the right compounds for each blended product. These needs were defined using the knowledge base, and also using existing products as a benchmark.

  Translate needs: The knowledge base is required to translate the needs.

  Set target values: The target values are justified according to the knowledge base.

- *Step 2: Structures generation*

  The input data were loaded into CAMD to generate the structures. The result summarizes the total number of compounds generated and selected, and total time used to design. The CAMD results give the compound structures, groups and occurrences, and the estimated target properties.

- *Step3: Compounds screening*

Identify the compounds: The CAPEC database is used to identify the compound's name, where it can be accessed from CAMD. If the compounds are not listed in the CAPEC database, then open databases were used for identification by giving their structures as input.

Retrieve physico-chemical properties and temperature-dependent model parameters: The pure component properties and temperature-dependent model parameters were retrieved from the CAPEC database and handbooks. ProPRED was used to predict the missing pure component properties.

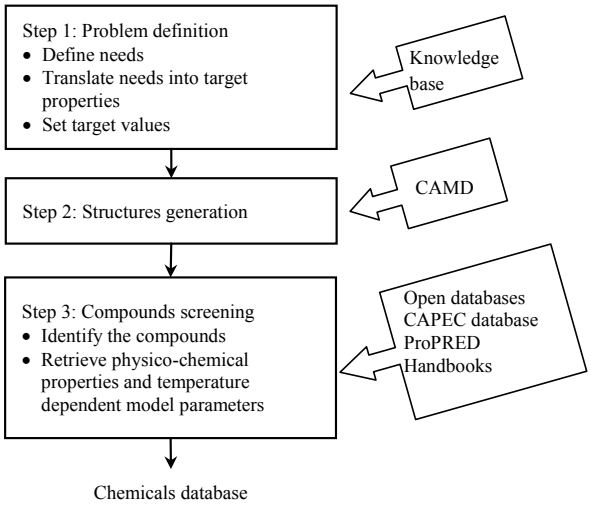

Figure 3.6 Work-flow of the additives database development

3.4.2 Gasoline database

The additives database for gasoline section contains chemicals that have potential as fuel substitutes. The database was developed as follows:

- *Step 1: Problem definition*

Database needs: Gasoline contains mostly, light components, where they must be stable, safe to be used in the internal-combustion engine and increase or at least

maintain the engine efficiency. Atoms or compounds that have a possibility to degrade the gasoline stability, reduce engine efficiency and are harmful to the environment are avoided. It is also important to ensure that the compounds are liquid at the ambient temperature.

Translate needs into target properties:

Light component : Molecular weight, Mw

Liquid at ambient temperature: Melting point, T_m

Stable, safe and enhance the engine efficiency: Choice of chemical types

Set target values: The limit of molecular weight was assumed according to the simplest hydrocarbon, methane and the average of gasoline molecular weight, (100±50 g/mol). Meanwhile, the upper limit of melting point is referring to the average ambient temperature, less than 293.15 K. Acyclic and cyclic compounds, aromatics, esters, ethers, aldehyde, ketones, acids, amines, amides and phenols groups were selected.

- *Step 2 :Structures generation*

The type of compounds and groups were specified, the target properties were selected and the constraints in CAMD were set, and the program was executed. As a result, 7,700 compounds satisfied the constraints.

- *Step 3: Compounds screening*

Identify the compounds: Of these 7,700 compounds, 273 are available in the CAPEC database. Meanwhile, the identities of the rest of the compounds were searched in open databases. The unidentified compounds were removed, which makes a total of 660 compounds selected for the gasoline database.

Retrieve physico-chemical properties and temperature-dependent model parameters: The pure component properties and temperature-dependent model parameters for 207 chemicals were retrieved from the CAPEC database. The missing properties were predicted using ProPRED.

The information of 660 compounds, their physico-chemical properties and obtained parameters were stored in the gasoline database section. These compounds were categorized according to their family. Meanwhile, compounds that can be produced from renewable sources were categorized as bio-based chemicals. 22 of them were listed as bio-based chemicals. Moreover, any compounds can be added if they are suitable as fuel substitutes.

3.4.3 Lubricant database

The additives database for lubricant section contains liquid chemicals that are suitable as lubricant, where they are designed as follows:

- *Step 1: Problem definition*

  Database needs: The compounds must be liquid at ambient temperature. Lubricants contain mostly heavy components, which should not easily vaporize and be retained as a liquid when they are applied in any lubrication systems. The compounds must also be safe to be handled by humans and to the environment as well.

  Translate needs into target properties:

  Liquid at ambient temperature: Melting point, Tm

  Heavy component : Molecular weight, Mw

  Not easily vaporize : Normal Boiling Point, T_{bp}

  Safe for human and the environment: Choice of chemical types

  Set target values: The upper limit of melting point is less than 293.15 K, while the lower limit of normal boiling point is greater than 303.15 K. These values are set by referring to the average ambient temperature. Meanwhile, the limit of molecular weight was assumed to have an average molecular weight greater than 150 g/mol. Meanwhile, acyclic and cyclic compounds, aromatics, esters, ethers, aldehydes, ketones, acids, amines, amides and phenols groups were selected.

- *Step 2 :Structures generation*

  The type of compounds and groups were specified, the target properties were selected and the constraints were set in CAMD, and the program was executed. As a result, 12,313 compounds were found to satisfy the constraints.

- *Step 3: Compounds screening*

  Identify the compounds: Most of the compounds were unknown, where only 11 of them were found in the CAPEC database. Therefore, open databases were used to identify them and 782 compounds were found available.

  Retrieve physico-chemical properties and temperature-dependent model parameters: The pure component properties and temperature-dependent model parameters were obtained from the CAPEC database, handbooks, as well as open databases. The missing properties were predicted using ProPred.

The information of 782 compounds, their physico-chemical properties and obtained parameters were stored in the lubricant database section. In addition, more hydrocarbons were added into the lubricant database, where they are identified in the CAPEC database and handbooks. These hydrocarbons were used to design mineral base oil. For the lubricant database, 25 chemicals were identified as bio-based chemicals, mostly derived from vegetable oils. Moreover, 150 polymers were also incorporated in the database, because polymers have high viscosity, which makes them suitable as additives in the lubricant blend design.

The details of the chemicals database are given in Table 3.6. The types of pure component properties are also provided in the table.

Table 3.6 Section of the database with numbers of available chemicals. The last column indicates the pure chemical property present in the database.

Section	Main Ingredient	Additives: number of compounds	Pure chemical property
Gasoline	Conventional gasoline	Bio-based: 22 Others: 660	Non temperature dependent; *Mw, Tc, Pc, ω, Z_{RA}, LC_{50}, T_f, ΔH_c, ON, Wt_{O2}* Temperature dependent: *ρ (15°C), μ (15°C), P_{sat}(38°C),*
Lubricant	Mineral oil Glycerol WCO Waste PE	Hydrocarbons: 913 Bio-based: 25 Polymers: 150 Others: 624	Non temperature dependent; *Mw, T_f, T_m, PP, δ, T_g, [η], $ρ_a$* Temperature dependent: *ρ(100°C), ρ(40°C), μ(100°C), μ(40°C), P_{sat}(25°C)*

WCO: waste cooking oil, PE: polyethylene

3.5 The mixture blend/design algorithm

The mixture/blend design algorithm employs a decomposition method, where the problem is decomposed into four sub-problems and solved accordingly as shown in Figure 3.7. The first level is for screening the pure component properties, and the second level is to analyze the mixture stability. The third and fourth levels are taking into account the linear and non-linear target properties, respectively.

The mixture/blend design algorithm is described below for the case of binary and ternary mixtures. It can also be extended to multi-component mixtures. The first compound in mixtures is specified as the main ingredient (*MI*), and it must exist in all mixtures. It can be a single compound or a mixture of compounds. A binary mixture is a combination of the *MI* and a compound *i* (B_i) from the database ($MI+B_i$), while a ternary mixture consists of *MI* plus two compounds, *i* and *j* from the database ($MI+B_i+B_j$). Subscripts *i* and *j* represent the number of both compounds. To avoid any repetition of formulations of the ternary mixture, the value of the subscript *j* must always be greater than the value of the subscript *i*.

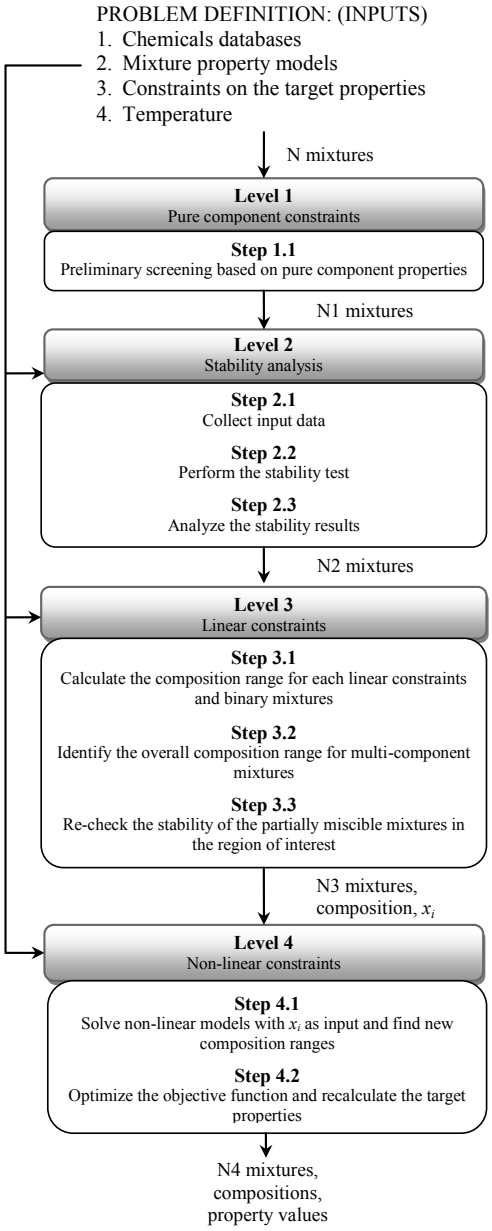

Figure 3.7 Mixture/blend design algorithm

3.5.1 Level 1: Pure components constraints

At this level, the pure component properties of chemicals in the database and *MI* were compared with respect to the target values. Note that, this step is applied only for the linear target properties.

Step 1.1: Compare the target property, ζ^k of the *MI* and the chemical(s) in the mixture with the target value boundaries, ζ_{LB} and ζ_{UB} for each target property *k*. Figure 3.8 illustrates the comparison of the binary mixture, where ζ_i^k represents the target property of chemical *i*; ζ_{MI}^k is the target property of *MI*; ζ_{LB}^k is the lower bound of the target property, *k*; and ζ_{UB}^k is the upper bound of the target property, *k*. This step is done for all possible mixtures that are considered in the design - binary, ternary or multi-component mixtures.

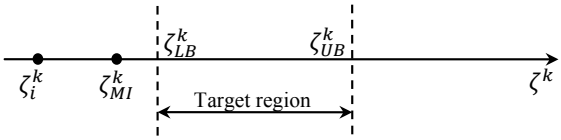

Figure 3.8 Representation of the property comparison. Binary mixture of *MI* and chemical *i* is infeasible.

Rule 1: Reject a binary mixture if the property value of *MI* and the pure component property value of the chemical *i* are both either lower than the lower bound values ($\zeta_{MI}^k < \zeta_{LB}^k$ and $\zeta_i^k < \zeta_{LB}^k$), or greater than the upper bound values ($\zeta_{MI}^k > \zeta_{UB}^k$ and $\zeta_i^k > \zeta_{UB}^k$). NR1 is the number of rejected binary mixtures.

Rule 2: Reject a ternary mixture if the property value of *MI* and pure component property values of the chemicals *i* and *j* are either lower than the lower bound values ($\zeta_{MI}^k < \zeta_{LB}^k$ and $\zeta_i^k < \zeta_{LB}^k$ and $\zeta_j^k < \zeta_{LB}^k$), or greater than the upper bound values ($\zeta_{MI}^k > \zeta_{UB}^k$ and $\zeta_i^k > \zeta_{UB}^k$ and $\zeta_j^k > \zeta_{UB}^k$). NR2 is denoted as number of rejected ternary mixtures.

Therefore, the number of remaining mixture is N1=N-NR1 for binary mixtures, and N1=N-NR2 for ternary mixture.

3.5.2 Level 2: Stability analysis

Step 2.1: Collect input data for the stability test. The input data consist of the UNIFAC-LLE group representation (Magnussen et al., 1981) of the chemicals involved in the mixtures, and the temperature at which the stability test has to be performed.

Step 2.2: Perform the stability test. The stability test of binary mixtures is performed using the STABILITY tool (Conte et al., 2011). The result obtained is the information on the miscibility of binary pairs indicated as either totally miscible, partially miscible or immiscible.

Step 2.3: Analyze the stability results. The result of the binary mixtures is obtained directly from the stability test. Also the stability result for a multi-component mixture is analyzed by first listing all binary mixtures that represent the multi-component mixture and then checking the stability of each binary pair. Total and partially miscible mixtures are considered for the next level of screening.

Rule 3: The multi-component mixtures are regarded as immiscible if any of the binary pairs to form them is found to be unstable. Reject the mixtures, which are immiscible to avoid any phase split of the blends.

3.5.3 Level 3: Linear constraints

Step 3.1: Calculate the composition range for each linear target property for all mixtures that satisfy the corresponding property target values. The composition-property relation for a binary mixture is illustrated in Figure 3.9.

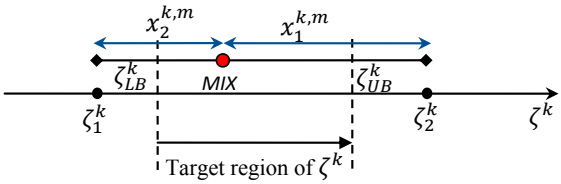

Figure 3.9 Representation of a binary mixture position

The composition ranges of chemical 1, $(x_{1,LB}^{k,m})$ and $(x_{1,UB}^{k,m})$ for a binary mixture, m is calculated as follows:

$$x_{1,LB}^{k,m} = \frac{\zeta_{UB}^{k,m} - \zeta_2^k}{\zeta_1^k - \zeta_2^k} \tag{3.37}$$

$$x_{1,UB}^{k,m} = \frac{\zeta_{LB}^{k,m} - \zeta_2^k}{\zeta_1^k - \zeta_2^k} \tag{3.38}$$

where, ζ_{UB}^k is the upper bound of the target property, *k*; ζ_{LB}^k is the lower bound of the target property, *k*; ζ_1^k and ζ_2^k are the target property values *k* of the chemicals 1 and 2, respectively. The specific composition, $x_1^{k,m}$ for a defined mixture is given by,

$$x_1^{k,m} = \frac{\zeta^{k,m} - \zeta_2^k}{\zeta_1^k - \zeta_2^k} \tag{3.39}$$

where $\zeta^{k,m}$ is the specific target value of property, *k*.

Step 3.2: Identify the overall composition range ($x_{1,LB}^m$ and $x_{1,UB}^m$) for each binary mixture by comparing the composition ranges of all target properties. The minimum and the maximum values of $x_{1,LB}^{k,m}$ and $x_{1,UB}^{k,m}$ calculated by Eqs. (3.37) – (3.38) for each property *k* are used as follows:

$$x_{1,LB}^m = max\left(x_{1,LB}^{k,m}\right) \tag{3.40}$$

$$x_{1,UB}^m = min\left(x_{1,UB}^{k,m}\right) \tag{3.41}$$

Rule 4: Reject any binary mixture, if $x_{1,LB}^m > x_{1,UB}^m$. NR4 is the number of mixtures that satisfy rule 4.

Rule 5: A ternary or multi-component mixture is assumed to be infeasible if any of the binary mixtures representing it is found to be infeasible. For example, if binary mixtures of $MI+B_1$, and $MI+B_2$ are rejected due to the implementation of rule 4, then the combination of them to form a ternary mixture of $MI+B_1+B_2$ is regarded as infeasible. *NR5* is the number of mixtures that are infeasible.

Steps 3.1 and 3.2 are combined and solved as a linear optimization problem to minimize and maximize the blend compositions (*x*) subject only to linear constraints as follows:

$$\text{min or max} \quad f_{obj}(x) \tag{3.42}$$

s.t.

$$\zeta_{LB} \leq g_2(x,\zeta) \leq \zeta_{UB} \tag{3.43}$$

$$g_3(x) = 0 \tag{3.44}$$

$$x \in \{x | x \in R^n, 0 \leq x \leq 1\} \tag{3.45}$$

where g_2 is a vector of inear constraints, and g_3 is a vector of mole or weight or volume fractions. The solution of the problem is a range of compositions for each blend within which all the linear property constraints are satisfied.

Step 3.3: Re-check the stability of the partially miscible mixtures in the region of interest. The miscible region of partially miscible mixtures is identified and compared with the region of interest. The overlap region is defined as a new region of interest, that gives a new composition range.

Rule 6: Reject the mixture that has a region of interest outside of the miscible regions.

3.5.4 Level 4: Non-linear constraints

Step 4.1: Calculate the non-linear mixture properties, $\zeta^{k,m}$ for the remaining binary mixtures at the overall composition range $x_{1,LB}^m < x_1^m < x_{1,UB}^m$ and find new composition ranges, ($x_{1,LB}^m$ and $x_{1,UB}^{k,m}$) that satisfy the non-linear constraints.

Rule 7: Reject the binary mixtures that do not match the non-linear target values, $\zeta^{k,m} < {\zeta_{LB}}^k$ and $\zeta^{k,m} > {\zeta_{UB}}^k$. *NR6* is the number of mixtures that were rejected after applying rule 7.

This step is solved as a non-linear optimization problem to minimize and maximize the blend composition (x) subject to both linear and non-linear constraints as follows:

$$\text{min or max} \quad f_{obj}(x) \tag{3.46}$$

s.t.

$$\zeta_{LB} \leq g_2(x,\zeta) \leq \zeta_{UB} \tag{3.47}$$

$$\zeta_{LB} \leq g_4(x,\zeta,\theta) \leq \zeta_{UB} \tag{3.48}$$

$$g_5(x) = 0 \tag{3.49}$$

$$x \in \{x | x \in R^n,\ x_{LB} \leq\ x \leq x_{UB}\} \tag{3.50}$$

where g_4 is a vector of the non-linear constraints whereas θ is the additional parameter required for non-linear constraints, such as temperature and activity coefficient, and g_3 is a vector of mole or weight or volume fractions. The composition, *x,* is restricted by lower and upper limits. As a result, new composition ranges are obtained, where the lower-bound value is not allowed to be lower than the specified bound and vice versa for the upper-bound. This ensures that all linear and non-linear property constraints are satisfied.

Step 4.2: In this step, the mixture compositions within the established bounds from step 4.1 that minimize (or maximize) the defined objective function Eq. (3.1) are determined. As a final test, the original optimization problem with all the constraints is solved with the bounds from step 4.1 and the optimal solution from above is used as the initial estimate.

N4 is the number of mixtures that satisfies the constraints at level 4. *N4= N3-NR6.*

At this point, all the mixtures that satisfy the linear and non-linear property constraints have been identified.

The input and output for the algorithm is summarized in Table 3.7.

Table 3.7 Summary of the mixture/blend design algorithm

Tasks	Input	Output	Methods /Tools
Step 1.1	Properties of the main ingredient, MI and chemicals Target values	Chemical pairs N1 mixtures	Comparison (MATLAB)
Step 2.1	List of chemicals	UNIFAC-LLE representation	Literature (Magnussen et al., 1981)
Step 2.2	UNIFAC-LLE representation Temperature	Binary pairs with their miscibility information and composition	STABILITY tool (Conte et al., 2011)
Step 2.3	Binary pairs with their miscibility information Chemical pairs from L1	Chemical pairs that are miscible or partially miscible N2 mixtures	Simulator – Analyzer (MATLAB)
Step 3.1 and 3.2	Chemical pairs from L2 Linear target properties of MI and chemicals Linear property models	Chemical pairs with the overall composition ranges	Simulator – Optimizer (*linprog* solver, MATLAB)
Step 3.3	Chemical pairs that are partially miscible with their composition and the overall composition ranges	Chemical pairs with the new composition ranges N3 mixtures	Simulator – Analyzer (MATLAB)
Step 4.1	Chemical pairs with their overall composition ranges Non-linear target properties of MI and chemicals Non-linear property models with their associate parameters Temperature	Chemical pairs with new composition ranges and estimated non-linear target values	Simulator - Optimizer (*fmincon* solver, MATLAB)
Step 4.2	Chemical pairs with new composition ranges Linear target properties of MI and chemicals Linear property models	Chemical pairs with new composition ranges and estimated linear target values N4 mixtures	Simulator - Calculator (MATLAB)

3.6 ICAS tools

The Integrated Computer Aided System (ICAS) software has been applied in many parts of this work. The ICAS consists of a number of toolboxes that help to efficiently solve a wide range problems. The chemical database is developed with aid of the Computer-Aided Molecular Design (CAMD) tool, the Property Prediction tool (ProPred), and the CAPEC database. CAMD was used to generate the molecular structures of the required chemicals as additives in the blend design, where their properties are obtained from the CAPEC database and some predicted using ProPred. ProPred is a powerful tool for the property estimation using a group contribution approach. Most of the physical and chemical properties are available through ProPred, including the environment-related properties. The STABILITY tool was used to check the stability test of the possible mixtures at the desired temperatures.

CHAPTER 4

CASE STUDIES

This chapter presents the case studies that were solved using the developed methodology and tools. The case studies are divided into two parts; the gasoline blend (§4.1) and lubricant blends (§4.2). Two design problems of gasoline blends were solved, which are the design of gasoline blends with bio-based chemicals and design of the gasoline blends with various chemicals. Meanwhile, four different lubricant design problems were solved. The first problems are dedicated to design the lubricant base oil, and the other two problems are to design of lubricant blends.

Gasoline blends:

- Gasoline blends with bio-based chemicals
- Gasoline blends with various chemicals

Lubricant blends:

- Base oil blends
- Base oil blends with polymer
- Lubricant blends of mineral oils and bio-based chemicals
- Lubricant blends of renewable base oils and various chemicals

4.1 Case study 1: Gasoline blends

The following two issues need to be considered among others: the first is related to the security (or availability) of crude oil supply and the second is related to the presence of toxic constituents in gasoline that are harmful to the environment as well as to humans. To address these issues, potential chemicals derived from renewable sources are being

blended with conventional gasoline. Adding bio-based chemicals can reduce the crude oil consumption and the amount of released toxic chemicals. The new formulation of gasoline blends should have good fuel performance, should be safe and have low environmental impacts.

4.1.1 Gasoline blend problem 1.1: Design of gasoline blends with bio-based chemicals

The aim of this case study is to design green gasoline. The latter will address issues related to the availability of raw materials to produce gasoline. The conventional gasoline was blended with potential chemicals derived from renewable sources, called bio-based chemicals. The bio-based chemicals available in the gasoline database are alcohols with low carbon number (C2 – C5), ethers, ketones, acid and furan derivatives.

The gasoline blends were designed for a car (spark-ignition type) engine and for a hot climate with average ambient temperature of 27^{o}C. The blends may consist of two or more chemicals (in addition to the gasoline chemicals) to form either binary or ternary mixtures. Besides reducing the crude oil consumption, the new formulation of gasoline blends should have good fuel performance, safe and low environmental impacts.

4.1.1.1 Task 1: Problem definition

Task 1.1 Identify product needs. Based on the knowledge base, the gasoline blend must have the following characteristics: can be burnt and run the engine efficiently; can flow continuously from the fuel tank to the combustion chamber; have a suitable flammability limit; and have low toxicity. In addition, the gasoline blends must be stable, meaning that the blends do not evaporate easily; do not oxidize to form unwanted by-products, such as gums, sludge and deposits during storage; and must not split into two liquid phases.

Task 1.2 Translate needs into physico-chemical properties. The product needs were translated into properties using the knowledge base. Table 4.1 lists the translated target properties.

Table 4.1 Product needs and translated target properties

Need	Target property
Ability to be burned	Reid vapour pressure (*RVP*)
Engine efficiency	Octane rating (*RON*) and heating value (*HHV*)
Consistency of fuel flow	Dynamic viscosity (η) and density (ρ)
Flammability	Flash point (T_f)
Toxicity	Lethal concentration (LC_{50})
Stability	Gibbs energy of mixing (ΔG^{mix})
Environmental aspect	Oxygen content (Wt_{O2})
Low oxidation	Choice of chemicals

Task 1.3 Set target values. The target values for each property were set as given in Table 4.2. These values were obtained from the existing products, legislation and previous literature (van Basshuysen and Schäfer, 2004; Forsythe, 2003).

Table 4.2 Target values for each target property

Need	Target property	Target value
Ability to be burned	*RVP*	$45 \leq RVP \leq 60$
Engine efficiency	*RON*	$RON \geq 92$
	HHV	$HHV \geq 40$
Consistency of fuel flow	η	$0.30 \leq \eta \leq 0.60$
	ρ	$0.720 \leq \rho \leq 0.775$
Flammability	T_f	$T_f \leq 300$
Toxicity	LC_{50}	$-logLC_{50} < 3.08$
Stability	ΔG^{mix}	$\Delta G^{mix} < 0$
Environmental aspect	Wt_{O2}	$2 \leq Wt_{O2} \leq 20$
Low oxidation	Choice of chemicals	

4.1.1.2 Task 2: Property model identification

Task 2.1 Retrieve the required property models from the property models library. Five of the target properties were estimated using linear mixing rules, which are η, *RON*, *HHV*, $-logLC_{50}$, and Wt_{O2}. The linear mixing model is represented by Eq. (3.13). The ρ, *RVP* and T_f were predicted using non-linear models, which are shown in Eqs. (3.14), (3.15) and (3.32), respectively.

4.1.1.3 Task 3: Mixture/blend design

Task 3.1 Collect input data. Conventional gasoline was selected as *MI* and its' composition is given in Table 4.3. The building blocks were selected from the gasoline database section, which are 22 bio-based chemicals derived from renewable sources.

Table 4.3 Pseudo-components of gasoline to represent the *MI*

Chemicals	Composition, wt%
Butane	6.58
Heptane	12.60
Iso-octane	53.99
1-pentene	3.63
Methylcyclopentane	8.47
Toluene	14.73

Task 3.2 Generate and screen blends using the mixture/blend design algorithm. The blending problem was solved using the mixture/blend design algorithm as shown in Figure 3.7.

- *Level 1: Pure component constraints*

Step 1.1: All the possible blends were screened by comparing the pure component property values with the target values. The properties evaluated in this step are heating value, viscosity, lethal concentration and oxygen content. The combinations of mixtures that have pure property values outside of the target value ranges were rejected. For instance, the lethal concentrations of gasoline and 2-methylpropanal are 3.33 mol/L and 3.94 mol/L, respectively. The upper limit of lethal concenration in gasoline blends is less than 3.08 mol/L. Applying rule 1, the blend of gasoline and 2-

methylpropanal was rejected as both the target property values were greater than the upper limit.

- *Level 2: Stability analysis*

Step 2.1: The UNIFAC-LLE group representations were obtained for 28 chemicals (including the *MI* components), and the temperature was set at the ambient temperature.

Step 2.2: The stability test was performed using the STABILITY tool and the results for 378 binary mixtures were retrieved.

Step 2.3: The results for binary and ternary mixtures were analyzed. Only 6 of the ternary mixtures were found to be partially miscible.

- *Level 3: Linear constraints*

Step 3.1: The blend composition ranges were calculated for all linear target properties: heating value, viscosity, octane number, lethal concentration and oxygen content. The composition ranges were obtained for binary mixtures.

Step 3.2: The overall composition ranges for multi-component blends were identified. The results of this step gave the feasible mixtures with their composition ranges.

Steps 3.1 and 3.2 are combined and solved as a linear optimization problem with the objective to minimize and maximize the blend composition subject to the linear constraints, Eq. (4.2) which represents *RON, HHV, η, ρ, -logLC_{50}* and Wt_{O2} to match the target given in Table 4.2.

$$\text{min or max} \quad f_{obj}(x) \tag{4.1}$$

s.t.

$$\zeta_{LB}^{k} \leq \sum_{i}^{NC} x_i \zeta_i^k \leq \zeta_{UB}^{k} \tag{4.2}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0 \tag{4.3}$$

$$0 < x_i < 1 \tag{4.4}$$

The solution of the problem leads to 8 blends and 112 ternary blends (note that this means the compounds of the model gasoline plus 1 extra chemical compound for binary and 2 extra chemical compounds for ternary blends, respectively) being selected for the next step, while 8 binary blends and 109 ternary blends were rejected.

Step 3.3: Re-check the stability w.r.t the partially miscibility of the blends in the region of interest. No partially miscible blends were found. All of them were rejected after considering the linear constraints in Steps 3.1 and 3.2.

- *Level 4: Non-linear constraints*

Step 4.1: The non-linear constraints - RVP is considered as the non-linear constraint. The compositions from level 3 were used as inputs in this step, and new composition ranges were obtained. This step was solved as a non-linear optimization problem where the objective functions were to be minimized and/or maximized subject to the linear and non-linear constraints, Eqs. (4.6 – 4.7), to match the target given in Table 4.2.

$$\text{min or max} \quad f_{obj}(x) \tag{4.5}$$

s.t.

$$\zeta_{LB}^{k} \leq \sum_{i}^{NC} x_i \zeta_i^k \leq \zeta_{UB}^{k} \tag{4.6}$$

$$\sum_{i=1}^{NC} \frac{x_i \gamma_i P_i^{sat}(308K)}{RVP_B} = 1 \tag{4.7}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0 \tag{4.8}$$

$$x_{LB} < x_i < x_{UB} \tag{4.9}$$

The solution of the above problem gives new composition ranges that satisfy the linear and the non-linear constraints. The flash point was calculated using Eq. (3.32) by giving input of the composition that satisfies the RVP. All the blend candidates were satisfying the flash point constraint. After this step, 45 ternary blends were removed, while a total of 75 binary plus ternary blends were retained. None of the blends were removed due to the calculated flash-point temperatures as they were all within the specified bound.

Step 4.2: The objective here is to obtain the minimum gasoline composition in the blend formulations. Since this value is already known from Step 4.1, this step is not necessary.

The number of blends generated and screened at each level is shown in Figure 4.1 for both binary and ternary mixtures.

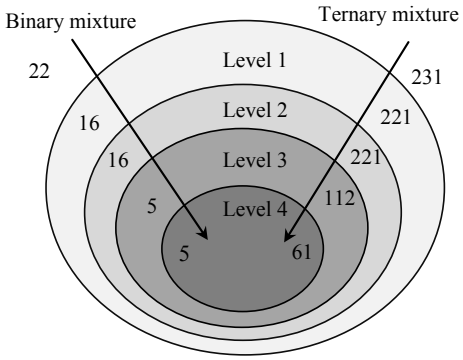

Figure 4.1 Number of gasoline blend candidates reduced after screening using mixture/blend design algorithm

Task 3.3 Rank blend candidates according to a selection criterion. The blends that satisfy all the constraints were ranked according to the maximum additives in blends. Table 4.4 highlights the binary and ternary mixtures, where the blends are listed in terms of decreasing gasoline composition.

4.1.1.4 Task 4: Verification

This task is not necessary for the final gasoline blends as the property models used were already validated with experimental data. What could be useful, however, is to have checked these blends under engine conditions, which is outside the scope of this work.

Table 4.4 Gasoline blended candidates with their composition and properties

n°	Composition (vol%)			Properties					
				HHV	$\boldsymbol{Wt_{O;}}$	***RVP***	***RON***	$\boldsymbol{\eta}$	$\boldsymbol{-logLC_{50}}$
	Binary mixture								
1	G (54)	MTBE(46)		40	8.4	57	-	0.41	2.7
2	G (54)	MSBE(46)		40	8.4	49	-	0.36	2.8
3	G (75)	MeTHF(25)		41	5.8	45	98	0.45	2.8
4	G (81)	THF (19)		40	5.0	50	-	0.47	2.8
5	G (92)	ETOH(8)		40	3.1	48	94	0.54	2.8
	Ternary mixture								
1	G (69)	THF (11)	MeTHF(20)	41	7.2	46	-	0.48	2.7
2	G (67)	ACE(13)	MeTHF(20)	41	7.8	46	-	0.47	2.7
3	G (72)	ACE(10)	2BE(18)	40	7.3	49	-	0.48	2.7
4	G (75)	2BE (13)	MeTHF(12)	43	5.5	45	-	0.50	2.9
5	G (77)	ETOH(12)	MeTHF(11)	42	6.7	45	96	0.57	2.8

4.1.1.5 Product analysis and discussion

The quality of fuel is measured from its energy content (*HHV*). Gasoline blends proposed in Table 4.4 have considerably high values of *HHV*. Their *HHV* values are close to the heating value of a conventional gasoline (44 – 47MJ/kg). *RON* is commonly used to measure the performance of fuel. Nevertheless, *RON* value cannot be predicted for some blends due to missing octane number for pure components, so the blends could not be further considered. Some of the binary formulations in Table 4.4 are not something new. Gasoline is commonly blended with MTBE and ethanol. MTBE is a well known antiknock additive for gasoline. However, due to the environmental concerns of the groundwater contaminant, MTBE is banned as a gasoline additive and replaced with ethanol. Nevertheless, ethanol content in gasoline is limited at below 10% for engine without modification. This is because the water content is high at a higher amount of ethanol, which causes phase separation in gasoline blend. Among the chemicals added in the gasoline blends, MeTHF becomes one of the favorable chemicals. It exists in most

candidates. MeTHF has good fuel properties, which are high-energy content, low vapor pressure, moderate oxygen level and considerable toxicity content. The properties of the blend candidates, then can be further validated through experimental work.

4.1.2 Gasoline blend problem 1.2: Design of gasoline blends with other chemicals

This case study is extended from the first case study by incorporating more options of the chemicals not limited only to bio-based chemicals. The objective of this case study is to find more suitable additives for gasoline blends. The gasoline blends are designed to fit the same purpose as the previous case study, which is to be used for a car (spark-ignition type) engine and in a hot climate with average ambient temperature of 27^{o}C. The same main ingredient was used and blended with various chemicals from the gasoline database.

4.1.2.1 Task 1: Problem definition

Since the same product is designed as the previous case study, the same procedures were performed for Tasks 1.1 – 1.3 (refer to § 4.1.1.1). Product needs, target properties and target values are given in Tables 4.1 and 4.2.

4.1.2.2 Task 2: Property model identification

Task 2.1 Retrieve the required property models from the property models library. The linear mixing rule, Eq. (3.13) was applied to predict η, HHV, $-logLC_{50}$, and Wt_{O2}, Eqs. (3.14), (3.15) and (3.32) were used to estimate RVP, T_f, and ρ, respectively.

4.1.2.3 Task 3: Mixture/blend design

Task 3.1 Collect input data. Conventional gasoline was selected as MI and its composition is given in Table 4.3. 221 chemicals were selected from the gasoline database section, which are from different groups of alkanes, alcohols, esters, ethers, ketones, acids, furans, etc.

Task 3.2 Generate and screen blends using the mixture/blend design algorithm. The blend candidates were generated and screened through the four-level mixture/blend design algorithm as shown in Figure 3.7. Initially, the number of possible blends is 221 binary and 24,310 ternary blends.

- *Level 1: Pure component constraints*

Step 1.1: All the possible blends were screened by comparing the pure component property values with the target values. Properties evaluated in this step are heating value, viscosity, lethal concentration and oxygen content. The combinations of the chemicals that have pure property values out of the target value ranges were rejected. Out of 221 candidate blends, 97 binary mixtures were rejected when applying rule 1, and 3642 of the ternary blends were removed after considering rule 2.

- *Level 2: Stability analysis*

Step 2.1: The UNIFAC-LLE group representation was obtained for all chemicals (including the *MI* components), and the temperature was set at the ambient temperature.

Step 2.2: The stability test was performed using the STABILITY tool and the results for all binary mixtures were retrieved.

Step 2.3: The results for binary and ternary mixtures were analyzed. 42 of the binary mixtures were found to be partially miscible with gasoline. All these mixtures were considered for Level 3.

- *Level 3: Linear constraints*

Step 3.1: Using the list of mixtures resulting from Step 2.1, the blend composition ranges were calculated for all linear target properties: heating value, viscosity, density, lethal concentration and oxygen content.

Step 3.2: Identify the overall composition range for multi-component blends. The results of this step gives the feasible mixtures and their composition ranges defined by lower- and upper-bounds.

Steps 3.1 and 3.2 were combined and solved as a linear optimization problem with the objective functions are aimed at minimizing and maximizing the blend composition, x subject to the linear constraint, Eq. (4.11), which represents the heating value, viscosity, density, lethal concentration and oxygen content to satisfy the target values given in Table 4.2.

$$\text{min or max} \quad f_{obj}(x) \tag{4.10}$$

s.t.

$$\zeta_{LB}^{k} \leq \sum_{i}^{NC} x_i \zeta_i^k \leq \zeta_{UB}^{k} \tag{4.11}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0 \tag{4.12}$$

$$0 < x_i < 1 \tag{4.13}$$

The result of the optimization problem rejected 86 binary and 14,362 ternary blends. The composition ranges were obtained for the remaining 38 binary and 6,306 ternary blends.

Step 3.3: Re-check the stability of the partially miscible mixtures in the region of interest. Six of the binary mixtures were identified as partially miscible. The region of interest was compared with the stability results for all partially miscible mixtures as given in Table 4.5. All the mixtures were rejected except mixture 1 because the region of interest is in the stable region. The same procedure was applied to determine the stability of the ternary mixtures and it was found that, 1471 ternary mixtures were partially miscible and 188 were rejected.

Table 4.5 Comparison of the region of interest and unstable region for the partially miscible binary mixtures. The highlighted row indicates the mixture is feasible.

n°	**Formulation**	**Region of interest**		**Unstable region**	
		x_1^{LB}	x_1^{UB}	x_1^{LB}	x_1^{UB}
1	G+C50*	0.8456	0.8485	0.0970	0.8110
2	G+C97	0.9059	0.9214	0.0270	0.9800
3	G+C100	0.6971	0.8437	0.0240	0.9800
4	G+C106	0.7953	0.8936	0.0290	0.9960
5	G+C121	0.6805	0.7685	0.3120	0.7790
6	G+C146	0.6922	0.6988	0.0660	0.9810

* C#: represent the number of chemical. Refers to the Table D.1 in the Appendix D, where the number of chemical is given at the first column, n°.

The total number of remaining mixtures after level 3 is 33 for the binary and 6118 for the ternary mixtures.

- *Level 4: Non-linear constraints*

Step 4.1: Calculate the non-linear constraints- the *RVP* is considered in this step. The compositions from the previous task were used as the input. New composition ranges were obtained after solving the non-linear optimization problem while the objective functions were to minimize and maximize the blend compositions, *x* subject to the linear and non-linear constraints Eqs. (4.15 – 4.16) to satisfy the target values given in Table 4.2.

$$\text{min or max} \quad f_{obj}(x) \tag{4.14}$$

s.t.

$$\zeta_{LB}^{k} \leq \sum_{i}^{NC} x_i \zeta_i^k \leq \zeta_{UB}^{k} \tag{4.15}$$

$$\sum_{i=1}^{NC} \frac{x_i \gamma_i P_i^{sat}(T)}{RVP_B} = 1 \tag{4.16}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0 \tag{4.17}$$

$$x_{LB} < x_i < x_{UB} \tag{4.18}$$

The optimization result gave new composition ranges. The flash point was calculated afterwards using Eq. (3.15) by giving a new composition as input. None of the blends were removed due to the calculated flash point. After considering both constraints, 28 binary and 4220 ternary blends were removed. At this point, all the blends were satisfied all the constraints. The reduced number of blend candidates is given in Table 4.6 for both binary and ternary mixtures.

Step 4.2: The objective here is to obtain the minimum gasoline composition in the blend formulations. Since the value is already known from Step 4.1, this step is not necessary.

Then, all the target properties were recalculated for all feasible mixtures using new compositions obtained from Step 4.2.

Table 4.6 Number of blend candidates that were retained from Level 0 – Level 4

Level	Number of binary mixture	Number of ternary mixture
Level 0	221	24,310
Level 1	124	20,668
Level 2	124	20,668
Level 3	33	6,118
Level 4	5	1,898

Task 3.3 Rank blend candidates according to a selection criterion. The blend candidates from Step 4.2 were ranked according to the minimum amount of gasoline in the blends. Table 4.7 gives the results, where the blends are listed in terms of decreasing gasoline composition.

4.1.2.4 Task 4: Verification

This task was is necessary for the final gasoline blends as the property models used were already validated with experimental data. What could be useful, however, is to check these blends under engine conditions, which is outside the scope of this work.

4.1.2.5 Product analysis and discussion

The results for the number of the gasoline blends were significantly reduced from Level 1 to Level 5. Only five of the binary blends were found to be feasible. The first three blends are mixtures of gasoline and a chemical containing a ketone group, while mixtures N^{o} 4 and 5 are gasoline blends with ethanol (C51) and methanol (C50). The amount of ethanol in the blend is less than 10%, which confirms that this is the suitable amount of ethanol that should be blended with gasoline. On the other hand, chemicals from the ketone group have potential as gasoline additives. The ketone has a carbonyl group, which is harmful to certain engine parts, such as elastomeric seals and diaphragms. Nevertheless, ketones have a good potential as fuel additives if the engine parts can be replaced with robust materials. Meanwhile, the ternary mixtures indicate that the gasoline blend can be achieved when more than half of the gasoline is replaced with additives. Ternary mixture N^{o} 1 also has high heating value. The top 20 blends were mostly mixtures of gasoline with ethers and alcohols, which are the most common additive types

blended with gasoline. Ethyl-tert-pentyl ether (C117) and diisopropylether (C102) are among the favorable additives in the ternary blends.

Table 4.7 Gasoline blend candidates with their composition and properties. Ranked according to gasoline composition, *x(1)*.

Nº	Formulation	Vol%		Properties						
		x(1)	*x(2)*	*HHV*	Wt_{O2}	*RVP*	ρ	η	$-logLC_{50}$	T_f
	Binary mixture									
1	G+C133*	0.8230	0.1770	4563	2.78	45.00	0.736	0.49	3.04	259.00
2	G+C135	0.8610	0.1390	4470	2.44	45.00	0.729	0.49	2.96	258.91
3	G+C137	0.8881	0.1119	4391	2.31	45.00	0.721	0.46	3.06	258.77
4	G+C51	0.9164	0.0836	4034	3.15	46.96	0.727	0.54	2.76	256.22
5	G+C50	0.9484	0.0516	4000	2.82	48.74	0.722	0.47	3.08	256.22
	Ternary mixture									
1	G+C88+C117	0.4709	0.0098	4637	7.48	50.93	0.769	0.50	2.81	237.64
2	G+C89+C117	0.4709	0.0098	4637	7.48	51.01	0.769	0.50	2.81	237.41
3	G+C90+C117	0.4709	0.0097	4637	7.48	51.04	0.769	0.50	2.81	237.52
4	G+C91+C117	0.4709	0.0097	4637	7.48	51.12	0.769	0.50	2.80	237.39
5	G+C92+C117	0.4709	0.0097	4637	7.48	51.01	0.769	0.50	2.80	237.54
6	G+C93+C117	0.4709	0.0097	4637	7.48	50.98	0.770	0.50	2.79	237.51
7	G+C33+C139	0.4825	0.1393	4699	4.59	60.00	0.742	0.54	2.74	237.41
8	G+C31+C176	0.4869	0.0508	4271	12.4	55.05	0.764	0.54	3.06	237.35
9	G+C89+C102	0.4903	0.0349	4326	7.97	47.20	0.740	0.44	2.65	237.27
10	G+C88+C102	0.4903	0.0246	4319	7.98	47.09	0.737	0.43	2.63	237.62
11	G+C93+C102	0.4904	0.0292	4322	7.97	47.17	0.740	0.44	2.58	237.44
12	G+C91+C102	0.4904	0.0251	4319	7.98	47.43	0.738	0.43	2.60	237.25
13	G+C90+C102	0.4904	0.0209	4317	7.98	47.30	0.737	0.43	2.62	237.45
14	G+C92+C102	0.4904	0.0207	4317	7.98	47.26	0.737	0.43	2.61	237.49
15	G+C33+C117	0.4910	0.0996	4467	5.87	50.18	0.738	0.45	2.85	237.47
16	G+C31+C117	0.4918	0.0595	4452	6.41	57.74	0.742	0.46	2.85	237.45
17	G+C76+C102	0.4950	0.0533	4250	8.97	51.86	0.764	0.46	2.55	236.67
18	G+C88+C116	0.4951	0.0103	4315	8.00	49.78	0.767	0.45	2.69	237.66
19	G+C89+C116	0.4951	0.0103	4315	8.00	49.86	0.767	0.44	2.69	237.31
20	G+C90+C116	0.4952	0.0102	4315	8.00	49.88	0.767	0.45	2.69	237.46

* C#: represent the number of chemical. Refers to the Table D.1 in the Appendix D, where the number of chemical is given at the first column, nº.

4.2 Case study 2: Lubricant blends

The lubricant case study is divided into two parts as shown in Figure 4.2. The first part of the lubricant case study is to design the base oil, which is the main component in lubricant. The base oil formulation obtained from part 1 is used as the base oil in the design of a suitable lubricant blend in the second part. The objective of this part is to find the formulation of the lubricant blends by mixing it with various chemicals in order to obtain the potential lubricant formulations. In this part also, the potential of several oils as base oils was discovered. Glycerol, waste cooking oil (WCO), and waste polymer possesses good attributes as a base oil, which can substitute the base oil from crude oil.

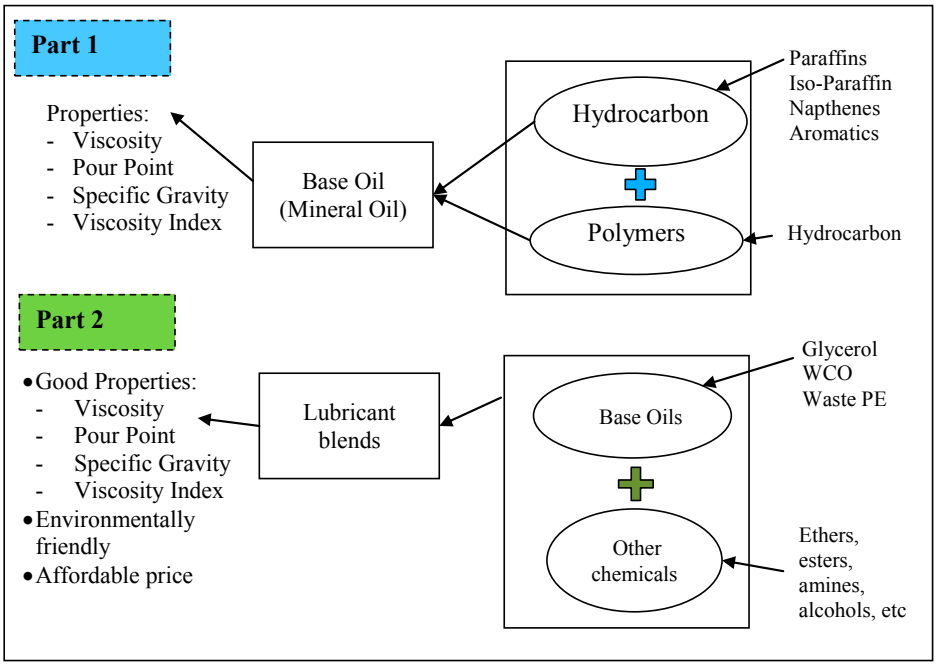

Figure 4.2 Blend formulation for lubricant case studies

4.2.1 Lubricant blend problem 2.1: Design of lubricant base oil

The mineral base oils are widely used as lubricant base oils. They are mixtures of complex hydrocarbons with different percentages of paraffins, naphthenes and aromatics. Therefore, the objective of this case study is to obtain the blend formulations to represent the mineral base oil. A set of hydrocarbons that consists of paraffins, naphthenes and

aromatics were selected as the components for blending. The formulations need to have a balance between all the components. A high content of paraffins makes mineral oil waxy, with a high melting point, which is suitable for high-temperature applications. Nevertheless, presence of aromatics and unsaturated chemicals causes excessive lubricant oxidation, which should be avoided.

4.2.1.1 Task 1: Problem definition

Task 1.1 Identify product needs. The needs for base oil were defined using the knowledge base. The main function of lubricant base oil is to lubricate and prevent wear between two moving surfaces. In addition, it must be able to resist a high temperature, flow continuously at a low temperature and non-flammable. Besides, the density of base oils is also observed for handling purposes.

Task 1.2 Translate needs into physico-chemical properties. The product needs were translated into properties using the knowledge base. The translated properties are given in Table 4.8.

Table 4.8 Base oil needs, the translated target properties and the target values

Needs	Property	Unit	Target value
Ability to lubricate and prevent wear	Viscosity, 100C	cSt	≥ 4.12
Resist at high temperature	Viscosity Index	-	≥ 80
Ability to flow at the ambient temperature	Pour point	K	≤ 273.15
Non-flammable	Flash point	K	≥ 493.15
Handling purpose	Density (ρ)	g/cm^3	0.80 – 0.90

Task 1.3 Set target values. The existing products (Kramer et al., 1999) were used as the benchmark in this design and the constraints were set for each property as given in Table 4.8. The viscosities for base oils are varied between 2 – 12 depending on the application ranges. Based on the average viscosity, 4.12 cSt was chosen as the lowest target value for the base oil design. The viscosity index (VI) is a scale used to measure the extent of viscosity change with temperature. VI greater than 80 was chosen. The pour point was

set as lower than 273.15 K. This is to ensure that the base oils are able to flow at the ambient temperature. Meanwhile, flash point greater than 493.15 K and density between 0.80 – 0.90 g/cm^3 were selected.

4.2.1.2 Task 2: Property model identification

Task 2.1 Retrieve the required property models from property model's library. Kinematic viscosity and density (molar volume basis) were estimated using liner mixing rules Eq. (3.13); viscosity index was estimated using Eq. (3.18); pour point was predicted using Eqs. (3.16) – (3.17); and flash point was calculated using Eq. (3.15).

4.2.1.3 Task 3: Mixture/blend design

Task 3.1 Collect input data. 913 hydrocarbons (paraffins, naphthenes and aromatics) are available in the lubricant database section. Hydrocarbons with molecular weight lower than 150 g/mol and viscosity less than 0.5 cSt were removed because they have only small significant effects in the mixture. A total number of 603 hydrocarbons was considered as building blocks for base oil mixture design. About 184 thousand binary mixtures and 37 million ternary mixtures can be formulated from the available chemicals. Note that, *MI* is not specified in this case study.

Task 3.2 Perform mixture/blend design algorithm. At Level 1 of the algorithm, the linear properties of viscosity and density were considered. Then the blend stability was checked at Level 2. The linear constraints, viscosity and density were estimated at Level 3, while the non-linear constraints, pour point, viscosity index, and flash point were calculated at Level 4.

- *Level 1: Pure component constraints*

Step 1.1: Viscosity and density of the chemicals forming the binary and ternary pairs were compared against the target values. About 98% and 97% of the binary and ternary mixtures were rejected at this level, respectively.

- *Level 2: Stability analysis*

Step 2.1: The input data consisting of the UNIFAC-LLE group representation for 603 hydrocarbons were collected, and two temperatures were set. First at the ambient temperature (298 K) and second was at the operating temperature (373 K).

Step 2.2: The stability test of binary mixtures was performed using the STABILITY tool. The results obtained are the information on the miscibility of binary pairs indicated as either totally miscible, partially miscible or immiscible.

Step 2.3: The results for binary mixtures were analyzed. All of the binary pairs were miscible. Therefore, all the ternary mixtures were also miscible. Thus, the number of mixtures remains the same.

- *Level 3: Linear constraints*

Step 3.1: The mixture composition ranges were calculated for all linear target properties: viscosity and density.

Step 3.2: The overall composition ranges were identified by comparing the composition ranges obtained for both target properties. The result of this step gives the feasible mixtures with their composition ranges defined by lower and upper bounds.

Steps 3.1 and 3.2 were combined and solved as a linear optimization problem with the objective to minimize and maximize the blend composition, x subject to the linear constraint, Eq. (4.20), which represents v and ρ to match the target values given in Table 4.8.

$$\text{min or max} \quad f_{obj}(x) \tag{4.19}$$

s.t.

$$\zeta_{LB}^{k} \leq \sum_{i}^{NC} x_i \zeta_i^k \leq \zeta_{UB}^{k} \tag{4.20}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0 \tag{4.21}$$

$$0 < x_i < 1 \tag{4.22}$$

The solution of the problem leads to 2790 binary and 244035 ternary mixtures being selected for the next step, while $660 \cdot 10^3$ ternary mixtures were rejected.

Step 3.3: Re-check the stability of the partially miscible mixtures in the region of interest. This step was skipped because all the mixtures were totally miscible.

- *Level 4: Non-linear constraints*

Step 4.1: The non-linear constraints – pour point and viscosity index were considered as non-linear constraints. The compositions obtained from Step 3.2 were used as input, and this step was solved as a non-linear optimization problem where the objective function, the blend composition, *x* is to be minimized and/or maximized subject to the linear and non-linear constraints, Eqs. (4.24 – 4.27), to match the target given in Table 4.8.

$$\text{min or max} \quad f_{obj}(x) \tag{4.23}$$

s.t.

$$\zeta_{LB}^{k} \leq \sum_{i}^{NC} x_i \zeta_i^k \leq \zeta_{UB}^{k} \tag{4.24}$$

$$BI_B = \sum_{i=1}^{n} x_{vi} BI_{PPi} \tag{4.25}$$

$$BI_{PPi} = PP_i^{1/0.08} \tag{4.26}$$

$$\frac{\nu_o - \nu_B}{\nu_o - \nu_{100}} \cdot 100 \geq VI_{LB} \tag{4.27}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0 \tag{4.28}$$

$$x_{LB} < x_i < x_{UB} \tag{4.29}$$

The solution of the above problem gives new composition ranges that satisfy the linear and the non-linear constraints. The flash point was calculated using Eq. (3.15) and the

composition that satisfied the *PP* and *VI*. All the blend candidates were found to satisfy the flash point constraint. After this step, 2776 binary and $1 \cdot 10^5$ ternary mixtures were removed, while 14 binary and $8.8 \cdot 10^4$ ternary mixtures were retained. None of the mixtures were removed due to the calculated flash-point temperatures as they were all within the specified bound. The number of mixtures generated and screened at each level is shown in Table 4.9.

Step 4.2: The objective function, Eq. (4.27) was optimized to obtain a high-viscosity base oil mixture. The new composition ranges obtained from Step 4.1, Eq. (4.28) were used as the upper and lower boundary. Then, the target property values for all feasible mixtures were recalculated using new compositions obtained from the optimization.

$$f_{obj} = \max \sum_{i}^{NC} x_i \ln v_i \tag{4.30}$$

$$x_{LB} < x_i < x_{UB} \tag{4.31}$$

Table 4.9 The reduced number of blend candidates using mixture/blend design algorithm

Level	Number of binary mixture	Number of ternary mixture
Level 0	183,921	$37 \cdot 10^6$
Level 1	2,790	$9 \cdot 10^5$
Level 2	2,790	$9 \cdot 10^5$
Level 3	2,790	$2 \cdot 10^5$
Level 4	14	$8.8 \cdot 10^4$

Task 3.3 Rank blend candidates according to a selection criterion. The mixtures that satisfy all the constraints were ranked according to their viscosity. Tables 4.10 – 4.11 give the shortlisted base oil mixtures for binary and ternary mixtures, which are listed in terms of decreasing viscosity.

Table 4.10 List of binary mixtures in order of decreasing viscosity, ν

N°	C1	C2	x_1	*v* (cSt)	*Mw* (g/mol)	*PP* (K)	*ρ* (g/cm^3)
1	cyclononadecane	cycloeicosane	0.54	5.43	273	273	0.847
2	cyclononadecane	1,1-diphenyltetradecane	0.88	5.31	276	273	0.857
3	cyclononadecane	1,1-diphenyldodecane	0.78	5.29	279	273	0.866
4	cyclononadecane	1,1-diphenylundecane	0.90	5.08	270	273	0.856
5	cyclononadecane	1,1-diphenyltetradecane	0.99	5.06	267	270	0.849
6	cyclononadecane	1,1-diphenyldodecane	0.99	5.05	267	269	0.849
7	cyclononadecane	cycloeicosane	0.99	5.05	267	269	0.848
8	1,1-diphenyloctane	cyclononadecane	0.01	5.02	266	269	0.849
9	1,1-diphenylheptane	cyclononadecane	0.01	5.01	266	269	0.849
10	cyclononadecane	2-undecylnaphthalene	0.99	5.00	267	270	0.849

Table 4.11 Shortlisted ternary mixtures with their properties

N°	C1	C2	C3	x_1	x_2	*v* (cSt)	*Mw* (g/mol)	*PP* (K)	*ρ* (g/cm^3)
1	cyclononadecane	cycloeicosane	1,1-diphenyl dodecane	0.55	0.44	5.42	273	273	0.848
2	cyclononadecane	cycloeicosane	1,1-diphenyl tetradecane	0.57	0.42	5.42	273	273	0.848
3	cyclononadecane	cycloeicosane	1,1-diphenyl decane	0.54	0.45	5.41	273	273	0.848
4	cyclononadecane	cycloeicosane	1,1-diphenyl undecane	0.57	0.42	5.39	273	273	0.848
5	cyclononadecane	1,1-diphenyl nonane	cycloeicosane	0.56	0.01	5.38	273	273	0.848
6	1,1-diphenyl heptane	cyclononadecane	cycloeicosane	0.01	0.55	5.37	272	273	0.848
7	1-octyl naphthalene	cyclononadecane	cycloeicosane	0.01	0.53	5.37	273	273	0.848
8	cyclononadecane	3-methyl octadecane	cycloeicosane	0.53	0.01	5.37	273	273	0.846
9	cyclononadecane	2,3-dimethyl heptadecane	cycloeicosane	0.53	0.01	5.36	273	273	0.847
10	2-heptyl naphthalene	cyclononadecane	cycloeicosane	0.01	0.53	5.36	272	273	0.848

4.2.1.4 Task 4: Model-based verification

All the base oil mixtures are ideal mixtures. Therefore, this task was not performed because, in principle, the linear mixing rule gives an acceptable prediction of the ideal mixtures.

4.2.1.5 Product analysis and discussion

There are many base oil formulations that satisfied all the given constraints. Viscosity was used as the selection criterion because viscosity is used to scale the grade of base oils. Viscosity also indicates the performance of the base oil. The formulation with highest viscosity is selected to represent the mineral oil formulation. Results show that the binary mixture consisting of cyclononadecane and cycloeicosane has the highest viscosity.

4.2.2 Lubricant blend problem 2.2: Design of high viscosity base oil

The objective of this case study is to formulate a high viscosity base oil. Blending of base oil with compounds that have high viscosity is one way to increase the viscosity. Such compounds usually possess high molecular weight like polymers. Therefore, the base oil is blended with polymers to enhance the viscosity of the base oil. The base oil was considered as the main ingredient, which was obtained from the previous case study. Meanwhile, hydrocarbon polymers were selected as the additives for the blending formulation.

4.2.2.1 Task 1: Problem definition

Task 1.1 Identify product needs. The needs for base oil blends were defined using the knowledge base. The main objective is to increase the viscosity of the base oil. The need to be achieved is high viscosity base oil. Nevertheless, other needs for lubricant must be achieved, such as resistance to high temperature and fluidity behavior. It also should have a suitable density for handling purposes. Besides, the base oil mixtures must be stable and do not oxidize to form deposits in the system.

Task 1.2 Translate needs into physico-chemical properties. Using the knowledge base the product needs were translated into properties as given in Table 4.12.

Task 1.3 Set target values. Referring to the existing products as benchmark and using the knowledge base, the target values for each property were set as indicated in Table 4.12 (Kramer et al., 1999).

Table 4.12 Needs, translated target properties and the target values for mineral oil blends with polymer.

Needs	Property	Unit	Target value
Ability to lubricate and prevent wear	Viscosity, 100C	cSt	4.12 – 12.5
Resist at high temperature	Viscosity Index	-	≥ 80
Ability to flow at the ambient temperature	Pour point	K	≤ 273.15
Handling purpose	Density (ρ)	g/cm^3	0.80 – 0.90

4.2.2.2 Task 2: Property model identification

Task 2.1 Retrieve the required property models from the property models library. A different set of property models is required to estimate the properties of blends involving polymers. The viscosity of the polymer solution is estimated using the Rudin and Strathdee method as given by Eq. (4.32) and for dilute polymer, φ is replaced with, φ_{sp}, Eq. (4.33) (Krevelen and Nijenhuis, 2009). The pure properties of polymer are slightly different with organic chemicals, for example, the pour point (*PP*) of polymer is assumed to be 3/2 of the glass transition temperature, T_g, and the volume of polymer refers to the amorphous volume. Density (molar volume basis) was estimated using linear mixing rules Eq. (3.13); viscosity index was estimated using Eq. (3.18); and pour point was predicted using Eqs. (3.16) – (3.17);

$$\frac{\eta_s}{\eta} = 1 - 2.5\varphi + 11\varphi^5 - 11.5\varphi^7 \tag{4.32}$$

$$\varphi_{sp} = \frac{0.4[\eta]c}{1 + 0.765[\eta]c - 1.91\frac{c}{\rho}} \tag{4.33}$$

4.2.2.3 Task 3: Mixture/blend design

Task 3.1 Collect input data. The main ingredient was selected from Table 4.10, which is a binary mixture of cyclononadecane+cycloeicosane. This mixture represents mineral oil, (MO). Meanwhile, 21 potential hydrocarbon polymers were selected from the polymer

database. Therefore, at the initial stage, 21 binary blends of mineral oil and polymers can be generated. Note that, only binary blends were considered in this work.

Task 3.2 Perform mixture/blend design algorithm. At Level 1 of the algorithm, the pour point of mineral oil and polymers were compared. Then the blend stability was checked at Level 2. In this case study, the viscosity was calculated first, even though it is a non-linear constraint. It is to ensure that the mineral oil blend achieves the target viscosity values. After that, the linear constraint, density was estimated at Level 3, while the non-linear constraints, pour point and viscosity index were calculated at Level 4.

- *Level 1: Pure component constraints*

  Step 1.1: In this case, only the glass transition temperature of polymer is compared with the target value. This is due to the fact that the polymers always have high viscosity, thus their glass transition temperatures need to be observed to make sure that the polymers are in liquid state at the design temperature. As a result, all polymers satisfied this constraint.

- *Level 2: Stability analysis*

  Step 2.1: The input data consisting of the solubility parameters, and molar volume of all chemicals and polymers, and were collected at a temperature, 298 K.

  Step 2.2: The stability test of binary mixtures was calculated using the Flory-Huggins method. The reduced Gibbs' energy of the mixtures were calculated, where the negative values indicate that the mixtures are miscibile. The stability result trends are shown in Figure 4.3.

  Step 2.3: The results for binary mixtures were analyzed. 9 of the binary mixtures were partially miscible. In this case, only totally miscible blends at both temperatures were considered. Therefore, 12 of the binary blends were found to have satisfied the stability constraint.

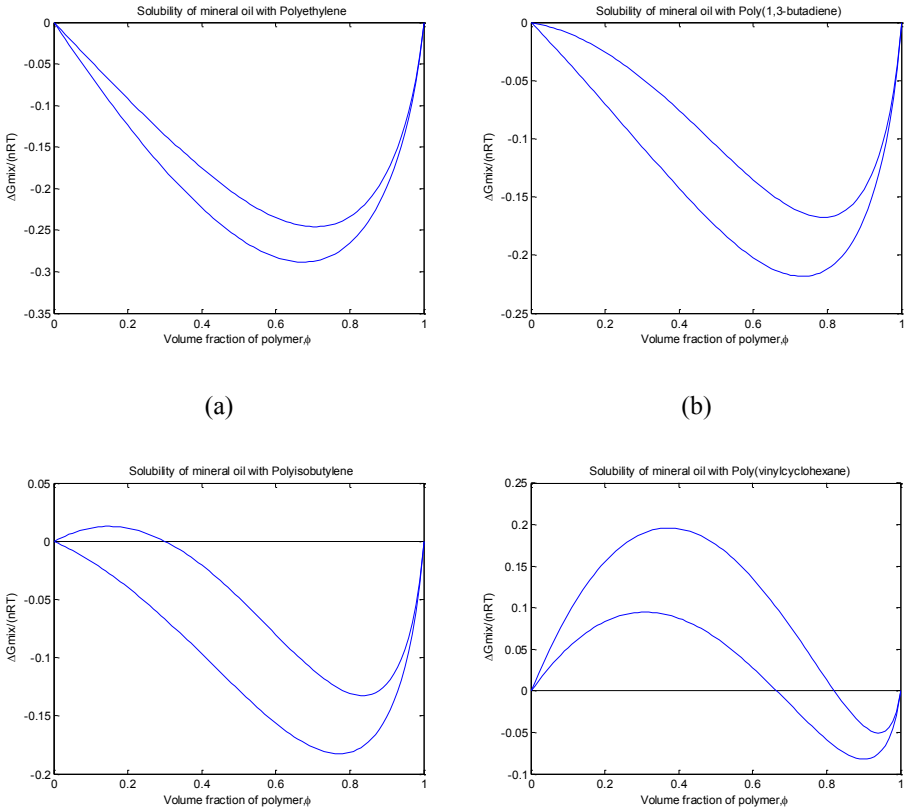

Figure 4.3 The stability results of the mineral oil (consists of two chemicals) blends with polymer at 298 K. Blends (a) and (b) are totally miscible, while (c) and (d) are partially miscible.

- *Level 3: Linear constraints*

Step 3.1: The mixture composition ranges were calculated for the viscosity. The composition range was obtained, then used to estimate the density.

Step 3.2: The overall composition range was determined using the optimizer tool, where the composition was optimized subject to linear constraint.

The optimization problem was solved when the composition ranges that satisfy the viscosity have been obtained. The objective is to minimize and maximize the blend composition, x subject to the linear constraint, Eq. (4.35), which represents only ρ to match the target values given in Table 4.8.

$$\text{min or max} \quad f_{obj}(x) \tag{4.34}$$

s.t.

$$\zeta_{LB}^{k} \leq \sum_{i}^{NC} x_i \zeta_i^k \leq \zeta_{UB}^{k} \tag{4.35}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0 \tag{4.36}$$

$$x_{LB} < x_i < x_{UB} \tag{4.37}$$

All the binary blends were selected for the next step, which means that the density constraint was satisfied.

Step 3.3: Re-check the stability of the partially miscible mixtures in the region of interest. This step was skipped because only totally miscible mixtures were considered.

- *Level 4: Non-linear constraints*

Step 4.1: The non-linear constraints – pour point and viscosity index were considered as the non-linear constraints. The compositions obtained from Step 3.2 were used as inputs, and this step was solved as a non-linear optimization problem where the objective function, the blend composition, x is to be minimized and/or maximized subject to the non-linear constraints, Eqs. (4.3 – 4.42), to match the target given in Table 4.12.

$$\text{min or max} \quad f_{obj}(x) \tag{4.38}$$

s.t.

$$\zeta_{LB}^{k} \leq \sum_{i}^{NC} x_i \zeta_i^k \leq \zeta_{UB}^{k} \tag{4.39}$$

$$BI_B = \sum_{i=1}^{n} x_{vi} BI_{PPi} \tag{4.40}$$

$$BI_{PPi} = PP_i^{1/0.08} \tag{4.41}$$

$$\frac{\nu_o - \nu_B}{\nu_o - \nu_{100}} \cdot 100 \geq VI_{LB} \tag{4.42}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0 \tag{4.43}$$

$$x_{LB} < x_i < x_{UB} \tag{4.44}$$

The solution of the above problem gives new composition ranges that satisfy the linear and the non-linear constraints. After this step, 3 binary blends were removed and 6 blends were retained.

Step 4.2: The objective of this step is to obtain high-viscosity base oil blends. However, this step was not performed due to the complexity of the model used to predict the viscosity of base oil and polymer blends. Nevertheless, the objective still can be achieved by selecting a high polymer composition in blends, which could directly influence the blend viscosity.

Task 3.3 Rank blend candidates according to a selection criterion. The mixtures that have satisfied all the constraints were ranked according to high polymer composition. Table 4.13 gives the shortlisted base oil blended with polymer.

4.2.2.4 Task 4: Model-based verification

This task was not performed because all the blends are ideal mixture. In principle, the linear mixing rule gives acceptable prediction of the ideal mixtures.

Table 4.13 Mineral oil blended formulations, with the mass fraction, (x) and their properties

N^o	Formulation	*x(1)*	*x(2)*	*ρ* (g/cm^3)	*PP* (K)	*v* (cSt)	Mw_{ave} (g/mol)
1	MO + Poly(1-butene)	0.72	0.28	0.8506	266	12.5	372
2	MO + Poly(2-methyl-1,3-butadiene)	0.72	0.28	0.8631	266	12.5	370
3	MO + Poly(1,3-butadiene)	0.72	0.27	0.8683	266	12.5	369
4	MO + Poly(1-pentene)	0.73	0.27	0.8478	266	12.5	367
5	MO + Polyethylene	0.73	0.26	0.8478	266	12.5	364
6	MO + Poly(2-methyl-1,3-butadiene)	0.77	0.23	0.8594	267	12.5	348

4.2.2.5 Product analysis and discussion

From the results in Table 4.13, it seems that the viscosity of mineral oils was improved by adding some amount of polymer. All the formulations achieved the upper limit of the target viscosity by adding less than 28% of polymer in the blends. Adding polymer in lubricant formulation could enhance the viscosity of the lubricant. Polymethacrylate (PMA) is one example of a viscosity modifier used in a high performance lubricant. At high temperature, polymer tends to melt, and therefore, also yielding an increase of the viscosity of the lubricant. In this case, however, only hydrocarbon polymers were considered. It can be extended further with other types of polymer in order to discover more potential viscosity enhancers for design of lubricant.

4.2.3 Lubricant blend problem 2.3: Design of engine oils for gasoline engine

The objective of this study is to design tailor-made lubricant blends, which are blends of mineral oils and bio-based chemicals that have good lubrication properties, as well as being environmentally friendly. The lubricant blend is designed specifically for gasoline engine oil. The lubricant blend is a formulation of base oil with additives. The most commonly used base oils in engine lubricants are mineral oils. Therefore, as the base case design, 44 basic chemicals of the mineral oils were pre-selected from the lubricant database section, including bio-based chemicals (given in the Appendix D). Superior additives are required for engine oil due to the higher demand of such an application. Blending of the mineral base oil and other chemicals not only reduce the consumption of fossil fuel, but also could enhance the lubricant attributes and lower the environmental impacts.

4.2.3.1 Task 1: Problem definition

Task 1.1 Identify product needs. The needs for engine oils were defined using the knowledge base. The main function of engine oil is to lubricate and prevent wear between two moving surfaces. Since engine oils are used to lubricate engine parts, they must be non-flammable and resistance of high temperature. The lubricant should also have a good transport property, where it can flow continuously at a low temperature. Besides, the density of base oils is also observed for handling purposes. Vapor loss to the surroundings is considered as one of the environmental issues, and thus it is taken into consideration during design.

Task 1.2 Translate needs into physico-chemical properties. The knowledge base was used to translate the product needs into appropriate target properties. The translated properties are given in Table 4.14.

Task 1.3 Set target values. The target values are different according to engine specifications, end-user applications and the standard set by ACEA (the Association des Constructeurs Europeens D' Automobiles) for European or API (American Petroleum Institute) for United States. The target values set in this case study were as refered to the European standard lubricant grade A1, which is suitable for gasoline engines at base performance (Rizvi, 2009). The target values are given in Table 4.14.

Table 4.14 Target properties and target values of engine oil

Needs	Property	Unit	Target value
Ability to lubricate and prevent wear	Kinematic viscosity@100°C	cSt	4.12－12.50
Resist high temperature	Viscosity Index	—	≥ 80
Ability to flow at the ambient temperature	Pour point	K	≤ 293
Handling purpose	Density @ 15°C	g/cm^3	0.80 － 0.98
Non-flammable	Flash point	K	≥ 493
Low vaporization rate	Evaporative loss @ 250 °C	%	≤ 15

4.2.3.2 Task 2: Property model identification

Task 2.1 Retrieve the required property models from the property models library. Kinematic viscosity and density (molar volume basis) were estimated using liner mixing rules Eq. (3.13); the viscosity index was estimated using Eq. (3.18); the pour point was predicted using Eqs. (3.16) – (3.17); the flash point was calculated using Eq. (3.15); and the vapor loss was evaluated using Eqs. (3.20) – (3.23).

4.2.3.3 Task 3: Mixture/blend design

Task 3.1 Collect input data. 44 basic chemicals, serving as base oil feedstocks, and bio-based chemicals were selected from the lubricant database section, and these chemicals were used as building block in the blend design.

Task 3.2 Perform mixture/blend design algorithm. At Level 1 of the algorithm, the linear properties of viscosity and density were considered. Then the blend stability was checked at Level 2. The linear constraints, viscosity and density were estimated at Level 3, while the non-linear constraints, pour point, viscosity index, flash point and vapor loss were calculated at Level 4.

- *Level 1: Pure component constraints*

Step 1.1: All the possible binary and ternary blends were screened by comparing their viscosity and density with their target values. 946 binary mixtures were screened and 901 were rejected. One example is the binary mixture of n-hexacosane+1,1'-Biphenyl, which was rejected due to the pure component viscosities.

- *Level 2: Stability analysis*

Step 2.1: The UNIFAC-LLE group representation is obtained for 44 chemicals, and the temperature is set at the ambient temperature and at the operating condition, 100^{o}C.

Step 2.2: The stability test was performed using the STABILITY tool and the results for binary pairs were extracted.

Step 2.3: The results for binary, ternary and multi-component mixtures were analyzed for both temperatures. 58 binary mixtures were partially miscible and 34 of the binary mixtures were found totally immiscible at one or both temperatures, and thus they were rejected. For example, the mixture of propane-1,2,3-triol + n-tetradecanoic acid was partially miscible at the ambient temperature. However, it was completely immiscible at 100^{o}C. Therefore, this mixture was not considered in the blend design.

- *Level 3: Linear constraints*

Step 3.1: Using the list of mixtures resulting from Step 2.1, the blend composition ranges are calculated for all linear target properties: Viscosity and density. The composition ranges are obtained for binary mixtures.

Step 3.2: Identify the overall composition range for multi-component (ternary and quaternary) blends. The results of this step are mixtures with their composition ranges.

Steps 3.1 and 3.2 are combined and solved as a linear optimization problem while the objective functions are to minimize and maximize the blend composition, *x* subject to the linear constraint, Eq. (4.46), which represents viscosity and density to match the target values given in Table 4.14.

$$\min \text{ or } \max \quad f_{obj}(x) \tag{4.45}$$

s.t.

$$\zeta_{LB}^{k} \leq \sum_{i}^{NC} x_i \zeta_i^k \leq \zeta_{UB}^{k} \tag{4.46}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0 \tag{4.47}$$

$$x \in \{x | x \in R^n, 0 \leq x \leq 1\} \tag{4.48}$$

Step 3.3: Re-check the stability of the partially miscible mixtures in the region of interest. Two partially miscible mixtures were identified and their stability regions were compared with the region of interest. One of the mixtures was rejected because it was found unstable at the region of interest, while the other was accepted because it was found to be totally miscible in the region of interest.

- *Level 4: Non-linear constraints*

Step 4.1: Calculate the non-linear constraints: Viscosity index, pour point, flash point and vaporization loss have been estimated and the new composition ranges are obtained. The compositions from the previous task are used as input in this step.

This step is solved as a non-linear optimization problem where the objective functions are to minimize and maximize the blend compositions, *x* subject to the linear and non-linear constraints, Eqs. (4.50) – (4.53) to satisfy the target property values given in Table 4.14. The flash point and vaporization loss were calculated for the blends that satisfied the non-linear constraints.

$$\text{min or max} \quad f_{obj}(x) \tag{4.49}$$

s.t.

$$\zeta_{LB}^k \leq \sum_i^{NC} x_i \zeta_i^k \leq \zeta_{UB}^k \tag{4.50}$$

$$BI_B = \sum_{i=1}^{NC} x_{vi} BI_{PPi} \tag{4.51}$$

$$BI_{PPi} = PP_i^{1/0.08} \tag{4.52}$$

$$\frac{\nu_o - \nu_B}{\nu_o - \nu_{100}} \cdot 100 \geq VI_{LB} \tag{4.53}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0 \tag{4.54}$$

$$x_{LB} < x_i < x_{UB} \tag{4.55}$$

About 51%, 7% and 68% of the binary, ternary and quaternary blends were removed at this level, respectively. A total number of 14, 966 and 5,483 of the binary, ternary and quaternary blends were found to satisfy all the constraints, respectively. The number of blends generated and screened at each level is listed in Table 4.15 for three types of blends.

Step 4.2: The objective function, Eq. (4.41) is optimized to obtain a low-cost base oil blend. The new composition ranges obtained from Step 4.1 were used as the upper and lower boundary. Then, the target property values for all feasible mixtures were recalculated using new compositions obtained from the optimization.

$$f_{obj} = \min \sum_{i}^{NC} x_i C_i \tag{4.56}$$

$$x_{LB} < x_i < x_{UB} \tag{4.57}$$

Task 3.3 Rank blend candidates according to a selection criterion. The price of the blend is used as the selection criterion. Since many blend formulations satisfy all the constraints, they were ranked according to the minimum price that is achievable for the selected purpose. The blends with lowest price for each type of mixture are given in Table 4.15.

Table 4.15 Blends formulation and their target properties at low cost

Blend	x_i	Cost ($/L)	Properties					
			ν	VI	PP	ρ	T_f	V_{vap}
Binary								
2MT + GLY	0.56 0.44	7.80	4.12	95	263	0.979	494	0
Ternary								
3ME + 3ET + GLY	0.08 0.54 0.38	6.88	4.12	101	273	0.978	565	0
Quaternary								
2MT + DFE + GLY + 9ODA	0.58 0.05 0.36 0.01	6.63	4.12	108	283	0.978	566	0

Note: Property abbreviations are given in the notations list

4.2.3.4 Task 4: Model-based verification

The viscosities of blends listed in Table 4.15 need further validation because all of them are non-ideal mixtures. The viscosities of the blends were estimated using a rigorous model and compared with the values estimated using a linear model. The comparison results are given in Table 4.16. The rigorous values are slightly higher than the linear values. Even so, the mixtures are still acceptable because the values obtained with the rigorous model are within the target range of 4.12 – 12.5 cSt. It should also be noted that, in general, viscosity has a wider range of permissible values.

Table 4.16 Comparison of the linear and rigorous viscosity values.

Mixture	Viscosity	
	ν-linear	**ν-rigorous**
Binary	4.12	4.4559
Ternary	4.12	4.4547

4.2.3.5 Product analysis and discussion

A mixture with low cost was selected for each type of mixture as listed in Table 4.15. The bio-based chemical, propane-1,2,3-triol (GLY) is present in all blends, while cis-9-Octadecenoic acid (9ODA) is present in blend 3. This indicates that the consumption of mineral base oil can be reduced by replacing it with base oil derived from renewable sources. As the price of bio-based chemicals is currently higher than mineral based oils, their blends also have higher prices. However, high viscosity indicates good quality of the lubricant, which is achieved in the blends listed in Table 4.15.

4.2.4 Lubricant blend problem 2.4: Design of lubricant blends using different type of base oils

In this case study, the potential of wastes and by-products as lubricant base oil were tested. They are glycerol, waste cooking oil and low polymer. The objective of this case study is to find the potential to replace the lubricant base oil with the above mention substitutes. The intended lubricant blend is for engine oils.

i. Glycerol is a by-product from production of biodiesel. Glycerol also called glycerin is a clear, colorless, odorless, hygroscopic and very sweet-tasting syrupy liquid, combustible, miscible with water, alcohol and acetic acid, and insoluble in ether, benzene and chloroform. The physical properties of glycerol satisfied the requirement as base oil except for cold flow properties. It has good viscosity, but poor cold flow properties, where it easily becomes solid at low temperature. Glycerol is suitable for high-temperature applications and closed system. It is unsuitable for open system because it tends to pick up moisture from the ambient air. The glycerol properties are shown in Table 4.17.

ii. On the other hand, many efforts have been put to turn waste cooking oil (WCO) into valuable products, such as biodiesel. WCOs become a pollution problem for some countries, especially in the Asia region. Therefore, in this work, the potential of WCO as lubricant base oil is discovered. WCO comprises a mixture of components. The composition varies depending on the sources of the cooking oil. The composition of WCO used in this work was obtained from Yaakob et al.,

(2013) as presented in Table 4.18. The WCO consists of a mixture of fatty acids and water as contaminants.

For the simplification of the blend design, only three components were considered. Components with a high-mass percentage were selected to represent the WCO composition, which are palmitic, oleic and linoleic acids. This WCO was assumed to undergo a pre-treatment process to remove any remaining moisture. Water should be removed because it will cause phase split in blending.

Table 4.17 Physical property of glycerol

Property	**Value**
Molecular weight	92.09 g/mol
Melting point	18.17 ºC
Boiling point	290 ºC at 1 atm
Density	1.261 g/cm^3 at 20ºC
Vapor pressure	0.33 Pa at 50 ºC, 26 Pa at 100 ºC
Viscosity	1499 cP at 20ºC (100% glycerol)
Kinematic viscosity	1189 cSt at 20ºC
Heat of combustion	1662 kJ/mol
Flash point	177ºC
Fire point	204ºC

Table 4.18 The composition of waste cooking palm oil

WCO component	**Mass Percent**
Palmitic Acid	8.5
Oleic Acid	21.2
Linoleic Acid	55.2
Stearic Acid	3.1
Linolenic Acid	5.9
Others	4.2
Water	1.9

iii. Low polymer (low molecular weight polyethylene) is a by-product in the production of high density polyethylene (HDPE). Usually, a low polymer is converted to polyethylene (PE) wax, which is for the manufacturing of candles, PVC pipes, as well as external and internal lubricant. Low polymer PE has a relatively low viscosity. Nevertheless, the existence of a small amount of HDPE in low polymer significantly affects the viscosity of low polymer, which is about 200 – 1200 cP. The high viscosity of low polymer causes a problem in converting low polymer to PE wax through a wax processing unit by removing remaining solvent and volatile compounds. A wax processing unit operates well for feed with a viscosity lower than 75 cP. Therefore, low polymer is always sold as a low-valued product. The low polymer is a mixture of polyethylene wax, soft wax and distillate as shown in Table 4.19. Distillate and soft wax are mixtures of straight chain hydrocarbon, where 80% of the distillate is n-hexane. Meanwhile soft wax consists of hydrocarbons with mostly C10 – C14.

Table 4.19 Physical properties of low polymer

Property	**Value**
Composition:	Mass percent (wt%)
Polyethylene wax	85
Soft wax	5
Distillate	10
Molecular weight	500 – 10,000
MWD, Mw/Mn	2 – 10
Melting point	120 – 126 ºC
Molar Volume (25ºC)	32.8 cm^3/mol
Viscosity	200 – 1300 cP
HansenD (δd)	16.463 $J^{1/2}$/ $cm^{3/2}$
HansenP (δp)	0
HansenH (δh)	0
Solubility par, δ (expt data)	15.8 – 17.1 $J^{1/2}$/ $cm^{3/2}$

In blend design, only the polyethylene wax is considered as the main ingredient. The properties of polyethylene are shown in Table 4.20 below.

Table 4.20 Physical properties of polyethylene

Properties	Value
Amorphous Density (g/cm^3)	0.85
Glass transition temperature, T_g (K)	195
Melting Point, T_m (K)	414.6
Intrinsic viscosity, $[\eta]_\Theta$ (cm^3/g)	1.06
SolPar[298K], δ (J/cm3)½	16.45

4.2.4.1 Task 1: Problem definition

The same type of product is designed as the previous case study. Therefore, the same procedures were performed for Tasks 1.1 – 1.3 (refers to § 4.2.3.1). Product needs, target properties and target values are given in Table 4.14

4.2.4.2 Task 2: Property model identification

Task 2.1 Retrieve the required property models from the property models library.

Kinematic viscosity and density (molar volume basis) were estimated using linear mixing rules Eq. (3.13); the viscosity index was estimated using Eq. (3.18); the pour point was predicted using Eqs. (3.16) – (3.17); the flash point was calculated using Eq. (3.15); and the vapor loss was evaluated using Eqs. (3.20) – (3.23). On the other hand, the viscosity for polymer mixtures was estimated using Eqs. (4.29 – 4.30).

4.2.4.3 Task 3: Mixture/blend design

This task was performed separately for each type of base oils.

Task 3.1 Collect input data. As *MI* either glycerol, WCO or low polymer was selected and 207 chemicals from the lubricant database section were selected as the additives. A total of 207 binary mixtures and 21,321 ternary mixtures can be formulated. Note that only binary mixtures were formulated for low polymer blends.

Task 3.2 Perform mixture/blend design algorithm. At Level 1 of the algorithm, the linear properties of viscosity and density were considered. Then the blend stability was checked at Level 2. The linear constraints, viscosity and density were estimated at Level 3, while the non-linear constraints, pour point, viscosity index, flash point and vapor loss were calculated at Level 4. For low polymer, the viscosity model is non-linear, which is considered at Level 4 only.

- *Level 1: Pure component constraints*

Step 1.1: All the possible binary and ternary blends of glycerol and WCO were screened by comparing their viscosity and density with their target values. Meanwhile, only density was considered for low polymer blends.

- *Level 2: Stability analysis*

Step 2.1: The UNIFAC-LLE group representations were obtained for all chemicals (including the *MI* components) that represent the glycerol and WCO blends. On the other hand, the solubility parameters, and the molar volume of all chemicals and polymers were collected at a temperature of 298 K.

Step 2.2: The stability test was performed using the STABILITY tool or the Flory-Huggins method (only for polymer blends) and the results for binary pairs were extracted.

Step 2.3: The results for binary pairs were analyzed. 36 binary pairs were totally immiscible with glycerol and 155 were partially miscible. The immiscible blends were rejected, while the partially miscible blends were considered for the next level. For the cases of WCO and polymer blends, 14 of the binary pairs were partially miscible with WCO, and 40 blends were partially miscible with polymer blends. They were rejected. Figure 4.4 shows the calculated excess Gibbs' energy of mixing for polymer blends.

- *Level 3: Linear constraints*

Step 3.1: The blend composition ranges were calculated for each linear target property: viscosity and density for glycerol and WCO blends, while only density is the linear constraint for polymer blends.

Step 3.2: The overall composition ranges were identified by comparing the composition ranges obtained for the related target properties.

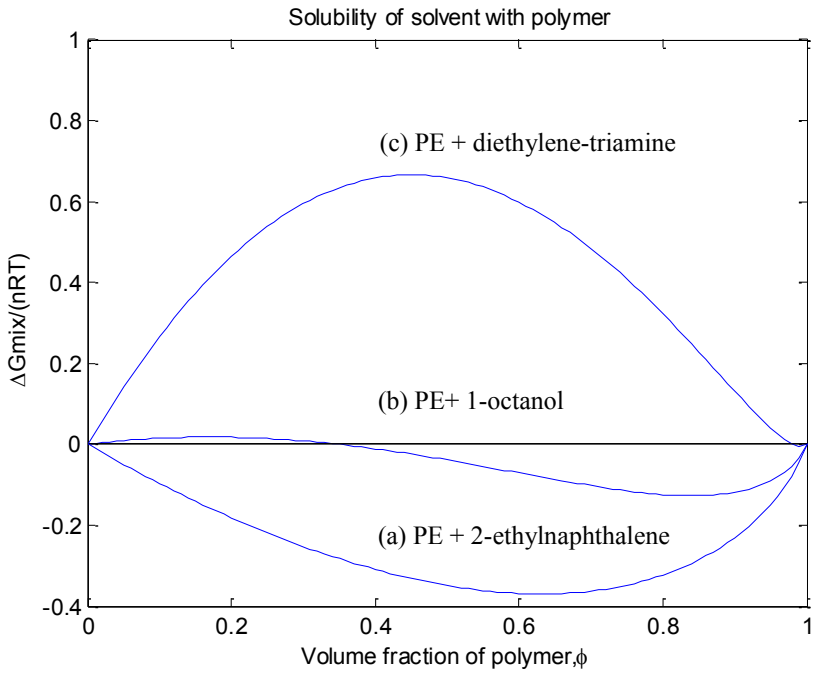

Figure 4.4 Excess Gibbs' energy of polymer blend. (a) is totally miscible, (b) is partially miscible, (c) is totally immiscible

Steps 3.1 and 3.2 were combined and solved as a linear optimization problem while the objective functions are to minimize and maximize the blend composition subject to the linear constraint, Eq. (4.59), which represents density and viscosity to match the target values given in Table 4.14.

$$\text{min or max} \quad f_{obj}(x) \tag{4.58}$$

s.t.

$$\zeta_{LB}^{k} \leq \sum_{i}^{NC} x_i \zeta_i^k \leq \zeta_{UB}^{k} \tag{4.59}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0 \tag{4.60}$$

$$x \in \{x | x \in R^n, 0 \leq x \leq 1\} \tag{4.61}$$

The problem solution gives blend formulations with the composition ranges that have satisfied the linear target properties.

Step 3.3: Re-check the stability of the partially miscible mixtures in the region of interest. In the glycerol case, 105 partially miscible mixtures were identified and their stability regions were compared with the region of interest. 63 of the mixtures were rejected because they were found unstable in the region of interest, while 42 blends were accepted.

- *Level 4: Non-linear constraints*

Step 4.1: Calculate the non-linear constraints: Viscosity index, pour point, flash point and vaporization loss have been estimated and the new composition ranges were obtained. The compositions from the previous task were used as inputs in this step.

This step is solved as a non-linear optimization problem where the objective functions are to minimize and maximize the blend compositions subject to the linear and non-linear constraints, Eqs. (4.63) – (4.66) to satisfy the target property values given in Table 4.14. The flash point and vaporization loss were calculated for the blends that have satisfied the non-linear constraints.

$$\text{min or max} \quad f_{obj}(x) \tag{4.62}$$

s.t.

$$\zeta_{LB}^k \leq \sum_i^{NC} x_i \zeta_i^k \leq \zeta_{UB}^k \tag{4.63}$$

$$BI_B = \sum_{i=1}^{NC} x_{vi} BI_{PPi} \tag{4.64}$$

$$BI_{PPi} = PP_i^{1/0.08} \tag{4.65}$$

$$\frac{\nu_o - \nu_B}{\nu_o - \nu_{100}} \cdot 100 \geq VI_{LB} \tag{4.66}$$

$$\sum_{i=1}^{NC} x_i - 1 = 0 \tag{4.67}$$

$$x_{LB} < x_i < x_{UB} \tag{4.68}$$

The number of blends generated and screened at each level is given in Table 4.21 for all cases.

Table 4.21 Number of blends generated and screened at each level for all cases

Level	**Glycerol blends**		**WCO blends**		**Low polymer blends**
	Binary	*Ternary*	*Binary*	*Ternary*	*Binary*
Level 0	207	21321	207	21321	207
Level 1	147	19551	207	21321	207
Level 2	112	12760	193	17846	167
Level 3	49	12760	193	17846	97
Level 4	0	0	0	277	87

Step 4.2: Since the objective of this case study is to find the potential base oil substitutes, composition is selected as the selection criterion. This task was not performed because the compositions were obtained from Step 4.1. The target property values for all feasible mixtures were recalculated using the highest compositions of the base oils.

Task 3.3 Rank blend candidates according to a selection criterion. The blends were ranked according to the highest composition of base oils, which are WCO and low polymer (PE). The blend formulations were listed in Tables 4.22 –4.23.

Table 4.22 List of feasible WCO blends with their properties

N°	Formulation	*x(1)*	*x(2)*	*v* (cSt)	*MW* (g/mol)	*PP* (K)	*ρ* (g/cm^3)
1	WCO + C153 + C154*	0.36	0.44	4.62	211.75	273.00	0.90
2	WCO + C153 + C160	0.36	0.44	4.79	214.47	273.15	0.90
3	WCO + C153 + C190	0.32	0.47	4.97	213.97	273.15	0.90
4	WCO + C153 + C201	0.31	0.48	5.14	215.52	273.15	0.90
5	WCO + C175 + C190	0.28	0.58	4.51	162.21	273.15	0.90
6	WCO + C175 + C201	0.27	0.59	4.60	162.44	273.15	0.90
7	WCO + C70 + C175	0.25	0.14	4.27	152.85	269.56	0.90
8	WCO + C69 + C175	0.25	0.14	4.26	152.90	269.54	0.90
9	WCO + C175 + C201	0.11	0.69	4.33	139.74	265.98	0.89
10	WCO + C175 + C190	0.11	0.70	4.30	136.43	265.09	0.89

* C#: represent the number of chemical. Refers to the Table D.3 in the Appendix D, where the number of chemical is given at the first column, n°.

Table 4.23 List of feasible PE blends with their properties

N°	Formulation	*x(1)*	*x(2)*	*ρ* (g/cm^3)	*PP* (K)	*v* (cSt)
1	PE + C49*	0.35	0.65	0.802	189.80	12.5
2	PE + C80	0.35	0.65	0.803	201.47	12.5
3	PE + C16	0.35	0.65	0.804	182.28	12.5
4	PE + C207	0.35	0.65	0.802	264.12	12.5
5	PE + C14	0.35	0.65	0.806	181.62	12.5
6	PE + C52	0.35	0.65	0.814	191.42	12.5
7	PE + C38	0.35	0.65	0.810	186.11	12.5
8	PE + C107	0.34	0.66	0.818	215.14	12.5
9	PE + C103	0.34	0.66	0.821	212.54	12.5
10	PE + C131	0.34	0.66	0.818	225.05	12.5
11	PE + C102	0.34	0.66	0.823	212.55	12.5
12	PE + C72	0.34	0.66	0.822	197.84	12.5
13	PE + C25	0.34	0.66	0.831	184.21	12.5
14	PE + C68	0.34	0.66	0.813	197.35	12.5
15	PE + C101	0.34	0.66	0.823	212.15	12.5
16	PE + C145	0.34	0.66	0.826	232.97	12.5
17	PE + C139	0.34	0.66	0.824	231.10	12.5
18	PE + C180	0.34	0.66	0.826	249.07	12.5
19	PE + C126	0.34	0.66	0.826	223.50	12.5
20	PE + C200	0.34	0.66	0.828	258.79	12.5

* C#: represent the number of chemical. Refers to the Table D.3 in the Appendix D, where the number of chemical is given at the first column, n°.

4.2.4.4 Task 4: Model-based verification

The models used are already validated with experimental data. Therefore, this task was not necessary for the final lubricant blends.

4.2.4.5 Product analysis and discussion

The results shown in Table 4.21 indicate that none of the glycerol blends have satisfied the non-linear constraints. This is because glycerol has a very high density and pour point. However, low values were required for the design of engine oil. Therefore, glycerol is unsuitable to be used as base oil for engine oil. Nevertheless, it has some advantages as a lubricant, possibly for other applications. In order to find formulations for other applications, the target values should be revised, and repeated Tasks 1 – 4.

WCO blends were obtained for ternary mixtures, where top 10 feasible candidates were listed in Table 4.22. The results indicate that chemicals C153 and C175 are the favorable chemicals. They are tetraethylenepentamine, and 1,5-pentanediol. Amines are usually used as additive in a lubricant, and have a function as antioxidants.

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

In this chapter, the achievements of this work are summarized (§5.1) and recommendations for future work are also given in (§5.2).

5.1 Achievements

The six main tasks have been identified (see §1.3) have been achieved as listed.

1. Formulate a general chemical blending problem in mathematical terms – done.
2. Identified the necessary property models and developed the required models – done.
3. Generate and identified the pure compounds of each design problem, where they were used as building blocks for blends design – done.
4. Developed mixture/blend design algorithm as a tool to solve the blending problems – done.
5. Developed a systematic methodology to design tailor-made blended products – done.
6. Applied the developed methodology through case studies: gasoline blends and lubricant blends – done.

The general formulation of blended product design was formulated as a mathematical problem, so that the blend problems can be solved using a model-based technique. The blending problem formed a MINLP problem.

The property model library was established for the problems under consideration. If the related property models were available in the literature, they were adopted in this work. They were verified in order to ensure that they were accurate for the studied systems. If the model was not available,a new property model is developed. In this work, GC property model is developed for prediction of the heat of combustion for pure components. The GC model gives a good prediction with R-squared value of 0.9999.

The chemical databases were developed for gasoline and lubricant blend designs, which contain petroleum-based and bio-based chemicals, as well as polymers. The knowledge base was also developed as a guide to design this type of products.

A mixture/blend design algorithm was developed, where it is used to generate and screen the blend candidates. The decomposition method was implemented, which efficiently solves the MINLP blending problem. The problem is decomposed into four sub-problems and solved according to their difficulty level. The least difficult problem with the largest search space is solved first, and then followed by the relatively more difficult problem with a reduced search space, and finally, the most difficult problem is solved for smallest search space.

A systematic methodology that integrates computer-aided methods was proposed. The methodology has four main tasks, where the blending problems were decomposed into sub-problems and solved sequentially. The methodology can be used at the initial stage of product design in order to find suitable candidates in blend formulations.

The systematic methodology for design of tailor-made blended products was applied on two case studies. The case studies show the capability of the developed methodology to handle a complexity in design of blended products. Two different problems were solved for gasoline blends while four different problems were solved for lubricant blends.

The work related to this PhD project was published in the journal publication and conference proceeding, and was presented in the conferences. The list of publications is presented in Appendix E.

5.2 Future work

In future, more work can be done to further improve the proposed methodology as well as to provide better platform in product design.

The knowledge base used in the problem definition is based on the information obtained from literature and existing products. The knowledge base was used to identify the need of the desired product, translate needs, and set the target values. The knowledge database can be further improved by involving experts in this area to share their knowledge and experiences. Therefore, a strong knowledge database can be established.

A chemical database was developed for each problem, where it contains different chemicals and related target properties. Chemicals stored in the database were generated using CAMD. The bio-based chemicals are, however, identified from literature and added in the database. More bio-based chemicals can be included in the database in future.

One of the limitations of the property models is the availability of the interaction parameters. New chemicals sometimes have a complex structure, which could not be described by the available groups. More effort should be focusing on the extension of the parameter tables, so that a wider problem can be considered in future.

The proposed blend formulations in the case studies need further experimental verification because the objective using the model-based approach is to give a good initial estimation for the experimental work. The target values may change in a real mixing process due to internal and external factors, nevertheless, the model-based approach is expected to give a very good idea of the final product.

The developed methods and tools were used separately during design of blended products. In order to make the blend design faster, the methods and tools can be implemented in a user friendly software in future. The virtual lab has been used to design formulated product. It can be extended to design different type of products by adding more work flows, more choice of property models, flexibility in database, in order to be able to handle various product designs at different complexity level.

APPENDICES

Appendix A

Data point for estimation of the HC

Table A. 1 Data points for estimation of the HC

n°	Compound	Exp	Est
1	1,2,3-Propanetriol	1655	1637
2	Hexadecanoic acid	9977	10022
3	Octadecanoic acid	11280	11328
4	1,2-Propanediol	1823	1827
5	Ethane, 1,1'-oxybis-	2732	2755
6	Ethanol	1368	1376
7	Benzoic acid	3227	3238
8	Methanol	726	723
9	2-Propanol	2006	2014
10	1-Propanol	2020	2028
11	1-Butanol	2676	2681
12	1-Pentanol	3330	3334
13	Benzene	3267	3394
14	Methanamine	1068	1145
15	Ethanamine	1715	1702
16	Oxirane	1263	1243
17	Methanamine, N,N-dimethyl-	2457	2477
18	Oxirane, methyl-	1889	1892
19	2-Propanamine, 2-methyl-	2996	3017
20	2-Propanol, 2-methyl-	2644	2687
21	Butane, 2,2-dimethyl-	4149	4181
22	2-Butanol, 2-methyl-	3303	3328
23	Butane, 2-methyl-	3504	3514
24	1-Propanamine, 2-methyl-	2996	2995
25	1-Propanol, 2-methyl-	2668	2668
26	2-Butanol	2661	2669
27	Butane, 2,3-dimethyl-	4155	4158
28	1,1'-Bicyclohexyl	7579	7641
29	Pentane, 3-methyl-	4160	4169
30	Acetic acid, hydroxy-, methyl ester	1429	1418
31	Cyclopentane, methyl-	3937	3954
32	Cyclopentanol	3097	3118

33	Benzene, methoxy-	3780	3777
34	Benzene, ethoxy-	4421	4430
35	Ethane, 1,1-diethoxy-	3871	3929
36	Octanoic acid, ethyl ester	6130	6156
37	Dodecanoic acid, ethyl ester	8778	8767
38	Hexanoic acid, methyl ester	4200	4197
39	Oxirane, ethyl-	2549	2563
40	2-Propen-1-ol	1854	1852
41	1,2-Ethanediol	1191	1186
42	Pentane, 2-methyl-	4158	4167
43	1-Butanamine, 3-methyl-	3639	3647
44	1,3 Butanediol	2495	2476
45	Butanoic acid	2184	2189
46	Pentane, 2,4-dimethyl-	4804	4806
47	Propane, 2,2'-oxybis-	4010	4004
48	Cyclohexane, methyl-	4565	4592
49	Benzene, methyl-	3910	3941
50	Cyclohexanol	3725	3756
51	Pentanoic acid	2836	2842
52	Propane, 1-(ethenyloxy)-2-methyl-	3818	3842
53	1-Butanamine	3001	3008
54	Ethanol, 2-methoxy-	1880	1904
55	Ethanamine, N-ethyl-	3035	3047
56	Ethene, ethoxy-	2540	2549
57	Decanoic acid, ethyl ester	7448	7461
58	Decanoic acid, methyl ester	6815	6808
59	Hexane	4163	4180
60	1,4-Butanediol	2498	2509
61	Ethane, 1,2-dimethoxy-	2624	2552
62	Cyclohexane	3919	3965
63	1-Propanamine, 2-methyl-N-(2-methylpropyl)-	5651	5632
64	Octanoic acid, methyl ester	5509	5503
65	Heptanoic acid	4145	4147
66	1-Hexanamine	4293	4313
67	1,5-Pentanediol	3154	3162
68	Butane, 1-(ethenyloxy)-	3859	3855
69	Propane, 1,1'-oxybis-	4031	4060
70	Ethanol, 2,2'-oxybis-	2374	2363
71	Octane	5470	5486
72	1-Heptanamine	4950	4966
73	1-Heptanol	4635	4639
74	Diethylene glycol methyl ether	3010	3048
75	Dodecanoic acid, methyl ester	8127	8114
76	Nonane	6125	6139
77	1-Octanol	5290	5292
78	Ethanol, 2,2'- 1,2-ethanediylbis(oxy) bis-	3558	3544
79	1-Decanol	6597	6598

80	Hexadecanoic acid, methyl ester	10669	10725
81	Dodecane	8087	8097
82	1-Undecanol	7254	7250
83	1-Dodecanol	7930	7903
84	Ethanol, 2,2'- oxybis(2,1-ethanediyloxy) bis-	4739	4729
85	Octadecanoic acid, methyl ester	11962	12030
86	1-Tetradecanol	9168	9209
87	1-Octadecanol	11820	11820
88	Eicosane	13316	13319
89	Methane, oxybis-	1460	1408
90	3-Buten-2-ol, 2-methyl-	3215	3147
91	Naphthalene, 1,2,3,4-tetrahydro-	5613	5618
92	Ethanamine, N,N-diethyl-	4366	4354
93	1-Butanol, 3-methyl-	3326	3321
94	1,4-Dioxane	2357	2346
95	Tetradecanoic acid, ethyl ester	10067	10072
96	Octanoic acid	4799	4800
97	Decane	6778	6791
98	Methanamine, N-methyl-	1771	1769
99	1,3-Propanediol, 2,2-dimethyl-	3131	3128
100	Acetamide, N,N-dimethyl-	2582	2588
101	1-Butanol, 2-methyl-	3326	3323
102	2-Propenoic acid, butyl ester	4047	4047
103	2H-Pyran, tetrahydro-	3143	3156
104	Heptane	4817	4833
105	Butane, 1,1'-oxybis-	5343	5366
106	Dodecanoic acid	7400	7411
107	1-Nonanol	5943	5945
108	Spiropentane	3277	3254
109	Cyclobutane	2720	2690
110	Cyclopentane	3291	3328
111	Cycloheptane	4598	4603
112	Cyclo-octane	5266	5240
113	Cyclononane	5931	5878
114	Cyclodecane	6586	6516
115	Propane, 2,2-dimethyl-	3493	3541
116	Butane, 2,2,3-trimethyl-	4804	4824
117	Cycloheptanol	4396	4394
118	1,3-Propanediol	1851	1856
119	1,3-Dioxane	2335	2346
120	2,3-Butanediol	2461	2473
121	Ethyl methyl ether	2107	2061
122	Pentane, 2,2,4-trimethyl-	5461	5473
123	Hexadecane	10699	10708
124	Methyl propyl ether	2737	2714
125	2-methylpropane-1,2-diol	2464	2479
126	Pentane, 3,3-dimethyl-	4804	4821

127	2,2,3-Trimethylpentane	5464	5479
128	Pentane, 2,3,4-trimethyl-	5466	5457
129	Hexane, 3,4-dimethyl-	5453	5468
130	Cyclohexanol, 2-methyl-	4380	4383
131	3-Pentanol	3312	3322
132	1,2-butanediol	2479	2480
133	2,3-dimethylhexane	5468	5466
134	Hexane, 3-methyl-	4813	4822
135	2,4-Dimethylhexane	5365	5461
136	Heptane, 3-methyl-	5468	5475
137	Pentane, 2,2-dimethyl-	4800	4834
138	1,1-Dimethylcyclohexane	5229	5253
139	2,2-Dimethylhexane	5459	5487
140	2,5-Dimethylhexane	5448	5459
141	Cyclopropane, methyl-	2719	2679
142	2,2,3,3-Tetramethylbutane	5452	5467
143	Methyl isopropyl ether	2751	2700
144	2-Butanol, 3-methyl-	3315	3313
145	2-Methyl-3-ethylpentane	5471	5461
146	3-Ethylpentane	4815	4822
147	Hexane, 3-ethyl-	5451	5475
148	Cyclohexane, 1,4-dimethyl-, cis-	5219	5218
149	Methyl n-butyl ether	3392	3366
150	Ethyl propyl ether	3379	3408
151	Hexadecanoic acid, ethyl ester	11368	11378
152	1,6-Hexanediol	3786	3814
153	Ethane, 1,2-diethoxy-	3909	3940
154	1,7-Heptanediol	4467	4467
155	Tridecane	8740	8750
156	Tetradecane	9394	9402
157	Pentadecane	10047	10055
158	1-Eicosanol	13130	13125
159	1,3-Dimethylcyclohexane	5212	5218
160	Pentane, 1,1'-oxybis-	6644	6671
161	Propanamide, N,N-dimethyl-	3237	3240
162	Butanamide, N,N-dimethyl-	3893	3893
163	Propane, 1-(ethenyloxy)-	3204	3202
164	1,2-Divinyloxyethane	3523	3578
165	Benzene, (ethenyloxy)-	4265	4249
166	1,2-Dimethylcyclopentane (trans-)	4584	4581
167	Propane, 2-(ethenyloxy)-	3187	3159
168	Pentane, 3-ethyl-3-methyl-	5468	5474
169	3,3-Diethylpentane	6125	6127
170	Pentane, 3-ethyl-2,4-dimethyl-	6130	6101
171	2,3,5-Trimethylhexane	6116	6105
172	2,2,4,4-Tetramethylpentane	6119	6140
173	Heptane, 2,2-dimethyl-	6112	6139

174	Octane, 2,7-dimethyl-	6747	6765
175	Undecane	7429	7444
176	2,2,3,4-Tetramethylpentane	6122	6123
177	Cyclopropane, ethyl-	3378	3351
178	1,2-Dimethylcyclopentane (cis-)	4590	4581
179	Xylene mixed	4547	4483
180	Cyclopentanol, 1-methyl-	3725	3726
181	Cyclopropane, 1,1-dimethyl-	3363	3340
182	Propane, 2-methoxy-2-methyl-	3364	3367
183	Cyclopentane, 1,1-dimethyl-	4583	4615
184	Ethylcyclopentane	4591	4626
185	Ethyl cyclohexane	5223	5263
186	n-Propylcyclohexane	5876	5916
187	Cyclohexane, butyl-	6530	6569
188	Cyclopentane, 1,3-dimethyl-, trans-	4585	4581
189	Cyclohexane, octyl-	9215	9180
190	Cyclohexane, decyl-	10451	10485
191	Cyclohexane, dodecyl-	11805	11791
192	n-octylcyclopentane	8581	8542
193	Cyclopentane, decyl-	9824	9848
194	n-Tetradecylcyclopentane	12533	12459
195	Cyclopentane, butyl-	5900	5931
196	Propylcyclopentane	5246	5279
197	cis-1,2-Dimethylcyclohexane	5222	5218
198	trans-1,3-Dimethylcyclohexane	5219	5218
199	trans-1,4-Dimethylcyclohexane	5212	5218
200	Cyclopentane, 1,3-dimethyl-, cis-	4587	4581
201	n-Nonylcyclopentane	9240	9177
202	Cyclobutanol	2518	2481
203	1,1,3-Trimethylcyclohexane	5882	5879
204	2,2,5-Trimethylhexane	6107	6126
205	Cyclopentane, pentyl-	6605	6584
206	Cyclopropane, 1,1,2-trimethyl-	3980	3967
207	Cyclopropane, 1,1,2,2-tetramethyl-	4636	4628
208	Cyclohexane, hexyl-	7898	7874
209	Cyclohexane, pentyl-	7239	7222
210	Hexylcyclopentane	7263	7237
211	3,4-Epoxyhexane	3818	3806
212	Cyclobutane, ethyl-	4017	3988
213	a-Trimethylethylene oxide	3133	3119
214	1,2-Pentanediol	3136	3128
215	Cyclohexane, heptyl-	8518	8527
216	n-Heptylcyclopentane	7922	7890
217	n-Dodecylcyclopentane	11216	11153
218	1,1'-Bicyclopropyl	3886	3815
219	Cyclohexane, tridecyl-	12509	12444
220	n-Tridecylcyclopentane	11875	11806

221	2-Pentanol	3315	3322
222	t-butylether	5320	5329
223	Cyclohexane, 1,1'-(1,4-butanediyl)bis-	10222	10263
224	N,N-Dimethylnonamide	7165	7157
225	Butane, 2,2'-oxybis-	5319	5314
226	trans-1,2-Dimethylcyclohexane	5217	5218
227	1,2-Hexanediol	3785	3781
228	2,2,3,3-Tetramethylpentane	6122	6107
229	1-Methoxydecane	7315	7283
230	Propane, 2-methyl-2-(1-methylethoxy)-	4648	4662
231	2-Butanamine	2994	3010
232	Nonane, 5-methyl-	6771	6780
233	Hexane, 2,2,4-trimethyl-	6117	6128
234	Hexane, 2,3,3-trimethyl-	6119	6117
235	Hexane, 2,4,4-trimethyl-	6120	6114
236	Hexane, 3,3,4-trimethyl-	6122	6119
237	Pentane, 3-ethyl-2,2-dimethyl-	6127	6128
238	Pentane, 2,3,3,4-tetramethyl-	6122	6107
239	Cyclopentane, 1-ethyl-1-methyl-	5241	5265
240	Cyclopentanol, 2-methyl-	3744	3745
241	1-hexadecanol	10476	10514
242	N-Undecylcyclohexane	11192	11138
243	1,1-dicyclohexylpentane	10930	10851
244	Cyclohexane, 1,1'-(1,5-pentanediyl)bis-	10930	10916
245	Cyclohexane, 1,1'-butylidenebis-	10220	10142
246	2,2-Dicyclohexylbutane	10240	10297
247	Propanoic acid	1528	1536
248	Benzene, (1,1-dimethylethyl)-	5858	5858
249	Benzene, 1,1'-methylenebis-	6923	6944
250	Benzene, 1,1'-(1,2-ethanediyl)bis-	7563	7564
251	Cyclohexene	3752	3783
252	Nonanoic acid	5454	5453
253	Bicyclo[4.3.0]nonane	5589	5622
254	1,4-Dimethylcyclohexane	5183	5218
255	1,3-Dimethylcyclohexane	5222	5218
256	Cyclohexene, 1-methyl-	4385	4345
257	Cycloheptene	4428	4421
258	Cyclopentene, 1-methyl-	3753	3708
259	Benzene, 1,1'-butylidenebis-	8907	8900
260	Benzene, 1,1'-(1,4-butanediyl)bis-	8885	8872
261	1-Propanone, 1-cyclohexyl-	5440	5471
262	1,1-Dicyclohexylethane	8638	8836
263	Cyclohexanone, 2,6-dimethyl-	4766	4790
264	Benzene, 1,1'-(1-ethyl-1,2-ethanediyl)bis-	8891	8870
265	Cyclohexanol, 2,6-dimethyl-	5044	5009
266	Dimethyl 2,6-naphthalenedicarboxylate	6528	6547
267	2-Propanamine	2355	2355

268	1,1'-Biphenyl -2-amine	6397	6402
269	1,2-Propanediamine	2512	2512
270	Cyclopropylmethylketone	2936	2926
271	Methacrylamide	2325	2330
272	Acetic acid	874	883
273	Phenyl glyoxylic acid	3518	3465
274	Hexanedioic acid	2797	2809
275	2-cyclohexen-1-one, 3,5-dimethyl-	4649	4565
276	Cyclohexanone, 3-methyl-	4196	4163
277	Cycloheptanone	4171	4172
278	Cyclohexanol, 3,5-dimethyl-	4991	5009
279	1,10-Decanediol	6393	6404
280	1,9-Nonanediol	5742	5773
281	1,8-octanediol	5094	5098
282	Tetradecanoic acid	8677	8717
283	Nonanoic acid, methyl ester	6177	6156
284	Tridecanoic acid, methyl ester	8792	8767
285	Cyclohexane, 1,1'-methylenebis-	8211	8305
286	1,3-Diphenylbutane	8912	8870
287	a-Methyldecalin	6851	6886
288	Cycloheptaneethanol	5661	5707
289	2-Methyl-1,2-propanediamine	3155	3157
290	Cyclopentanone, 3-methyl-	3516	3526
291	Heptanal	4444	4436
292	Butanal	2478	2478
293	Propanal	1817	1825
294	Propanal, 2-methyl-	2468	2468
295	2-Butenal	2286	2287
296	2-Hexenal, 2-ethyl-	4888	4890
297	Methacrolein	2293	2291
298	2-Ethylacrolein	2947	2945
299	Octanal	5100	5089
300	cyclohexanone	3518	3537
301	2-Butanone	2440	2442
302	Acetylacetone	2655	2661
303	2-Octanone	5060	5053
304	3-Octanone	5052	5064
305	2-Pentanone	3099	3094
306	Acetone	1788	1799
307	3-Penten-2-one, 4-methyl-	3557	3564
308	Ethyl acetoacetate	3160	3150
309	Methyl acetoacetate	2488	2497
310	1,3-Butadiene	2522	2513
311	1,3-Butadiene, 2,3-dimethyl-	3815	3824
312	1,5-Hexadiene	3863	3827
313	1-Decene	6620	6615
314	1-Octene	5313	5309

315	1-Heptene	4655	4657
316	1-Pentene, 2,4,4-trimethyl-	5291	5313
317	1-Pentene, 2,4-dimethyl-	4638	4646
318	1-Pentene, 4,4-dimethyl-	4645	4657
319	1-Pentene, 3-ethyl-2-methyl-	5297	5297
320	2-Pentene, 2,4-dimethyl-	4632	4627
321	trans-1,2-di-tert-butylethylene	6586	6609
322	2-Pentene, 2,4,4-trimethyl-	5292	5294
323	1-Butene, 2-ethyl-3-methyl-	4641	4644
324	2-Pentene, 4,4-dimethyl-, (E)-	4634	4653
325	3-Hexene, 3-methyl-, (Z)-	4639	4646
326	3-Hexene, 3-methyl-, (E)-	4643	4646
327	3-Hexene, 2,2-dimethyl-, (Z)-	5298	5307
328	(Z)-2,5-Dimethylhex-3-ene	5279	5276
329	1-phellandrene	6014	6046
330	Cyclohexene, 1-methyl-5-(1-methylethenyl)-, (R)-	6136	6132
331	1,3-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-	5985	6038
332	Limonene	6128	6132
333	1-Heptyne	4571	4571
334	Ethyl propiolate	2659	2660
335	2-Nonyn-1-ol	5614	5670
336	2-Octyn-1-ol	4993	5017
337	2-Butynedioic acid, diethyl ester	4010	4002
338	2-Nonynoic acid	5159	5178
339	Ethyl 2-octynoate	5838	5912
340	2-Nonynoic acid, ethyl ester	6495	6565
341	2-Octyne, 1,1-diethoxy-	7492	7038
342	2-Octynoic acid	4536	4525
343	Non-2-ynoic acid propyl ester	7192	7217
344	Dimethyl phthalate	4702	4672
345	1,2,3-Benzenetriol	2627	2626
346	Styrene	4402	4369
347	Phenylethyne	4290	4257
348	Phenylpropiolic acid	4277	4259
349	4-Phenyl-3-butyn-2-one	5173	5175
350	Ethylphenylpropiolate	5606	5645
351	3-Phenyl-2-propyn-1-ol	4765	4751
352	Propiolic acid, 3-phenyl-, methyl ester	5010	4993
353	Isovalerylphenylacetylene	7208	7121
354	1-Phenylpenta-1-yn-3-one	5805	5829
355	β-Phenylpropiolophenone	7487	7526
356	1-Phenyloct-2-yn-1-ol	7964	8065
357	Phenylpropiolamide	4589	4591
358	α-Methylstyrene	5045	5010
359	Benzene, (1,2-dimethyl-1-propenyl)-	6329	6306
360	Stilbene, α-methyl-, (E)-	8113	8123
361	Benzene, (1-methyl-1-propenyl)-, (E)-	5746	5745

362	Acetophenone	4142	4151
363	Acetamide, 2-cyano-	1577	1492
364	Acetic acid, cyano-, methyl ester	1978	1981
365	Methoxyacetonitrile	1218	1684
366	Acetonitrile, ethoxy-	2461	2378
367	3-Methoxypropionitrile	2458	2337
368	Ethyl cyanoacetate	2638	2634
369	Benzenamine,N-methyl-	4075	4040
370	Aniline	3396	3410
371	N,N-Diethylaniline	6072	6047
372	Diphenylamine	6424	6449
373	Benzenamine, N,N-dimethyl-	4761	4742
374	Benzene, 1-propenyl-	4797	4762
375	Benzaldehyde	3527	3494
376	Propanenitrile, 2,2-dimethyl-	3214	3214
377	3-Methylenecyclobutanenitrile	3569	3578
378	Cyclobutanecarbonitrile	3071	3043
379	Cyclohexanecarbonitrile	4274	4318
380	Cyclopropanecarbonitrile	2431	2406
381	2-Propenenitrile	1758	1758
382	Isobutyronitrile	2561	2552
383	Acetonitrile	1258	1288
384	Acetic acid, butyl ester	3505	3530
385	Isobutyl acetate	3534	3517
386	Isopropyl acetate	2874	2874
387	Benzamide	3551	3518
388	Formic acid, propyl ester	2217	2216
389	Butanedioic acid, 2,3-dihydroxy- R-(R*,R*) -, diethyl ester	3877	3882
390	Propanoic acid, 2-methyl-, 2-methylpropyl ester	4847	4845
391	Acetic acid, dichloro-, 1-methylethyl ester	2616	2635
392	Butanoic acid, 2-methyl-, butyl ester	5505	5513
393	Dichloroacetic acid butyl ester	3281	3301
394	Acetic acid, trichloro-, 1-methylethyl ester	2496	2494
395	Trichloroacetic acid butyl ester	3165	3160
396	Propanoic acid, 2,2-dimethyl-, ethyl ester	4183	4207
397	Acetic acid, trichloro-, ethyl ester	1876	1855
398	3-Pentanone, 2,2,4,4-tetramethyl-	5723	5734
399	3-Pentanone, 2,4-dimethyl-	4403	4423
400	3,5-Heptanedione, 2,6-dimethyl-	5301	5307
401	Ethanone, 1,2-di-2-furanyl-2-hydroxy-	4661	4659
402	8-Quinolinol, 5,7-dibromo-	4172	4161
403	Chloroxine	4145	4171
404	Iodoquinol	4350	4336
405	Cloxyquin	4299	4305
406	3-Methyl-1,2-butadiene	3212	3205
407	Phenyl formate	3343	3311
408	Ioxynil octanoate	8020	8035

409	1-Naphthalenol, acetate	5833	5833
410	2-Propanamine, N-(1-methylethyl)-	4330	4322
411	2-Butanamine, N-(1-methylpropyl)-	5636	5632
412	Benzalaniline	6864	6822
413	Acetaldehyde, phenylhydrazone	4436	4472
414	2-Propanone, phenylhydrazone	5095	5086
415	1,3-Benzenedicarbonitrile, 2,4,5,6-tetrachloro-	3437	3390
416	1,2-Benzenedicarbonitrile	3998	4001
417	1,4-Benzenedicarbonitrile	3988	3997
418	1,3-Benzenedicarbonitrile	3992	4000
419	Benzene, 2,4-diisocyanato-1-methyl-	4235	4211
420	Phenyl isocyanate	3422	3500
421	Benzene, 1-chloro-2-isocyanato-	3272	3342
422	1,3-dinitropropane	1823	1822
423	1,2-dinitroethane	1183	1169
424	1-Nitropentane	3324	3327
425	1-Nitrobutane	2668	2675
426	Propane, 1-nitro-	2010	2022
427	Ethane, nitro-	1359	1369
428	2-Nitrobutane	2653	2635
429	1,1-dinitropropane	1871	1901
430	Propane, 2-nitro-	1999	1980
431	Ethane, 1,1,2,2-tetrafluoro-1,2-dinitro-	602	604
432	Propane, 2-methyl-2-nitro-	2630	2623
433	2,2-dinitropropane	1848	1877
434	Methane, tetranitro-	433	408
435	Benzenamine, 2,4,6-trinitro-N-(2,4,6-trinitrophenyl)-	5497	5473
436	Benzene, 2-methoxy-1,3,5-trinitro-	3296	3289
437	Benzene, 1,3,5-trinitro-	2758	2794
438	2,4,6-Trinitrobenzoic acid	2774	2750
439	Benzene, 2-methyl-1,3,5-trinitro-	3410	3453
440	3-methyl-2,4,6-trinitrophenol	3213	3212
441	Nitramine	3500	3520
442	2-methyl-2-propylnitrit	2654	2681
443	Nitrous acid, 1-methylethyl ester	2017	2014
444	Nitrous acid, 1-methylpropyl ester	2672	2669
445	Nitrous acid, 2-methylpropyl ester	2675	2667
446	1-Propyl nitrite	2030	2027
447	Nitrous acid, butyl ester	2678	2680
448	1,3-Propanediol, 2,2-bis (nitrooxy)methyl -, dinitrate (ester)	2571	2574
449	propatylnitrate	3454	3462
450	1,2,3-Propanetriol, trinitrate	1529	1505
451	Ethanol, 2,2'-oxybis-, dinitrate	2285	2284
452	1-Propyl nitrate	1966	1987
453	Ethyl nitrate	1311	1334
454	Ethanediamide	863	863
455	Butanediamide	2136	2137

456	Butanamide	2496	2522
457	Acetamide	1187	1216
458	Propanamide	1990	1869
459	Pentanamide	3160	3174
460	Hexanamide	3795	3827
461	Octanamide	5104	5133
462	Propanamide, N-methyl-	2540	2530
463	Acetamide, N-methyl-	1868	1878
464	Glycine, N-glycyl-	1973	1984
465	Propanal, 2-(hydroxyimino)-, oxime	1915	1922
466	Methanone, diphenyl-, oxime	6811	6848
467	2-Butanone, oxime	2727	2679
468	Ethanone, 1-phenyl-, oxime	4414	4437
469	2-Propanone, oxime	2052	2027
470	Hydroperoxide, 1,1-dimethylethyl	2728	2743
471	Hydroperoxide, 1-methyl-1-phenylethyl	5108	5107
472	Cyclohexyl hydroperoxide	3803	3803
473	Ethyl hydroperoxide	1402	1437
474	Urea, tetraethyl-	5933	5975
475	Urea, tetramethyl-	3420	3364
476	Diacetamide	2088	2076
477	Acetamide, N,N-diethyl-	3884	3876
478	Carbonic acid, diethyl ester	2694	2657
479	Carbonic acid, diphenyl ester	6144	6173
480	2,5-Furandione, 3,4-dimethyl-	2637	2691
481	2-cyclopropen-1-one, 2,3-diphenyl-	7636	7514
482	Hypoxanthine	2429	2426
483	Xanthine	2160	2106
484	Urea, (2,5-dioxo-4-imidazolidinyl)-	1711	1711
485	Adenine	2779	2773
486	Uric acid	1922	1939
487	Guanine	2498	2440
488	Hydrazinecarbothioamide	1724	1705
489	Benzamide, 2-hydroxy-N-phenyl-	6380	6379
490	N-Benzoylbenzamide	6836	6811
491	Acetamide, N-(2-methylphenyl)-	4897	4917
492	2,4-Dimethylacetanilide	5502	5526
493	Acetamide, N-(4-methylphenyl)-	4921	4912
494	Acetamide, N-(3-methylphenyl)-	4922	4915
495	2-CHLOROPROPANOIC ACID	1395	1397
496	1-Propanol, 2,3-dichloro-	1713	1705
497	Propane, 1,2,3-trichloro-	1733	1742
498	Butane, 1,2-dichloro-	2533	2552
499	Propane, 2-chloro-2-methyl-	3328	2683
500	Butane, 2-chloro-2-methyl-	2675	3323
501	Acetic acid, dichloro-	622	619
502	Ethane, 1,1-dichloro-	1247	1278

503	Propane, 2,2-dichloro-	1880	1891
504	Propane, 1,2,2,3-tetrachloro-	1595	1578
505	Acetic acid, trichloro-	494	482
506	Methane, tetrachloro-	363	361
507	Ethane, 1,1,1-trichloro-	1110	1141
508	Ethane, 1,1,1,2-tetrachloro-	974	984
509	Propanoic acid, 3-iodo-	1435	1436
510	Butane, 2-bromo-	2705	2711
511	Propane, 1-bromo-	2057	2070
512	Propane, 2-bromo-	2052	2056
513	Butane, 1,2-dibromo-	2570	2559
514	1-Fluoro nonane	5963	5975
515	Heptane, 1-fluoro-	4692	4670
516	Dodecane, 1-fluoro-	7922	7934
517	2,2-difluoroethanol	1028	1042
518	1-Propanol, 2,2,3,3-tetrafluoro-	1353	1355
519	Acetic acid, difluoro-	563	576
520	1,2-Hydrazinedicarboxaldehyde	1028	1029
521	Benzamide, N,N-dimethyl-	4949	4906
522	1,4-Naphthalenedione	4606	4623
523	9(10H)-Anthracenone	6858	6844
524	Cyclohexanone, 5-methyl-2-(1-methylethylidene)-, (R)-	5933	5919
525	Glycine, N-(aminoiminomethyl)-N-methyl-	2324	2313
526	4H-Imidazol-4-one, 2-amino-1,5-dihydro-1-methyl-	2348	2348
527	Guanidine, nitro-	877	892
528	Cyclohexane, ethylidene-	5045	5046
529	Cyclopentane, ethylidene-	4413	4408
530	1,2,3-Propanetriol, monoacetate	2488	2490
531	Cyclohexanone, oxime	3751	3763
532	p-Benzoquinone oxime	2985	2970

Appendix B

Group contributions

Table B.1 – B.3 list the first-, second-, and third- order groups and their contributions (C_i, D_j, and E_k)

Table B. 1 First-order group and their results of heat of combustion regression

n°	Group	C_i	n°	Group	C_i
1	CH3	710.6822	111	CHCl2	419.6583
2	CH2	652.8408	112	CCl2	324.3614
3	CH	580.8447	113	CCl3	283.0019
4	C	525.2059	114	CH2F	548.5652
5	CH2=CH	1189.974	115	CHF	/
6	CH=CH	1123.013	116	CF	/
7	CH2=C	1126.251	117	CHF2	376.3941
8	CH=C	1050.741	118	CF2	311.5809
9	C=C	929.7846	119	CF3	/
10	CH2=C=CH	/	120	CCl2F	/
11	CH2=C=C	1639.183	121	HCClF	/
12	C=C=C	/	122	CClF2	/
13	CH#C	1100.365	123	aC-Cl	385.6876
14	C#C	978.178	124	aC-F	/
15	aCH	538.4012	125	aC-I	467.5494
16	aC	399.9674	126	aC-Br	381.4072
17	aC	397.3153	127	-I	-41.5529
18	aC	427.6102	128	-Br	-92.1701
19	aN	27.1429	129	-F	-52.7236
20	aC-CH3	1099.849	130	-Cl	-68.7572
21	aC-CH2	1018.153	131	CHNOH	604.7123
22	aC-CH	960.2365	132	CNOH	460.1132
23	aC-C	886.4103	133	aC-CHNOH	/
24	aC-CH=CH2	1537.044	134	OCH2CH2OH	1047.03
25	aC-CH=CH	1216.084	135	OCHCH2OH	/
26	aC-C=CH2	1463.915	136	OCH2CHOH	880.6803
27	aC-C#CH	1424.81	137	-O-OH	-74.0418
28	aC-C#C	1393.622	138	CH2SH	/
29	OH	-133.374	139	CHSH	/

30	aC-OH	283.0087	140	CSH	/
31	COOH	29.64564	141	aC-SH	/
32	aC-COOH	400.4017	142	-SH	/
33	CH3CO	940.9921	143	CH3S	/
34	CH2CO	886.1574	144	CH2S	/
35	CHCO	854.5179	145	CHS	/
36	CCO	773.7204	146	CS	/
37	aC-CO	601.9136	147	aC-S-	/
38	CHO	314.1967	148	SO	/
39	aC-CHO	661.768	149	SO2	/
40	CH3COO	716.2019	150	SO3	/
41	CH2COO	670.4049	151	SO3	/
42	CHCOO	622.7423	152	SO4	/
43	CCOO	552.4029	153	aC-SO	/
44	HCOO	55.23446	154	aC-SO2	/
45	aC-COO	476.3314	155	PH	/
46	aC-OOCH	478.5473	156	P	/
47	aC-OOC	387.4624	157	PO3	/
48	COO	55.80484	158	PHO3	/
49	CH3O	579.9135	159	PO3	/
50	CH2O	508.9432	160	PHO4	/
51	CH-O	435.3591	161	PO4	/
52	C-O	369.4254	162	aC-PO4	/
53	aC-O	227.0833	163	aC-P	/
54	CH2NH2	844.967	164	CO3	-213.609
55	CHNH2	788.9688	165	C2H3O	1036.068
56	CNH2	726.1977	166	C2H2O	940.134
57	CH3NH	914.1429	167	C2HO	844.4036
58	CH2NH	828.5846	168	CH2	636.575
59	CHNH	755.4197	169	CH	552.0927
60	CH3N	908.3372	170	C	501.1813
61	CH2N	771.9928	171	CH=CH	1090.157
62	aC-NH2	564.7919	172	CH=C	962.264
63	aC-NH	490.5506	173	C=C	923.2941
64	aC-N	483.2256	174	CH2=C	1171
65	NH2	280.7074	175	NH	60.94454
66	CH=N	435.1056	176	N	291.4052
67	C=N	337.1119	177	CH=N	586.512
68	CH2CN	1069.598	178	C=N	323.6866
69	CHCN	988.6958	179	O	-174.637
70	CCN	925.2833	180	CO	207.63
71	aC-CN	852.2943	181	S	/
72	CN	427.7807	182	SO2	/
73	CH2NCO	/	183	>NH	202.0493

74	CHNCO	/
75	CNCO	/
76	aC-NCO	651.8008
77	CH2NO2	511.2786
78	CHNO2	415.0691
79	CNO2	333.9698
80	aC-NO2	372.6305
81	NO2	-24.3763
82	ONO	-134.521
83	ONO2	-175.806
84	HCON(CH2)2	/
85	HCONHCH2	/
86	CONH2	353.5316
87	CONHCH3	1021.018
88	CONHCH2	953.5631
89	CON(CH3)2	1730.365
90	CONCH3CH2	/
91	CON(CH2)2	-200.814
92	CONHCO	2310.514
93	CONCO	/
94	aC-CONH2	685.6153
95	aC-NH(CO)H	/
96	aC-N(CO)H	/
97	aC-CONH	679.4712
98	aC-NHCO	809.1779
99	aC-(N)CO	/
100	NHCONH	/
101	NH2CONH	470.8711
102	NH2CON	/
103	NHCON	/
104	NCON	375.28
105	aC-NHCONH2	/
106	aC-NHCONH	/
107	NHCO	/
108	CH2Cl	553.6404
109	CHCl	487.0853
110	CCl	386.1564

184	-O-	/
185	-S-	/
186	>CO	/
187	PO2	/
188	CH-N	/
189	SiHO	/
190	SiO	/
191	SiH2	/
192	SiH	/
193	Si	/
194	(CH3)3N	/
195	N=N	/
196	Ccyc=N-	568.2352
197	Ccyc=CH-	1005.675
198	Ccyc=NH	291.4052
199	N=O	/
200	Ccyc=C	973.3155
201	P=O	/
202	N=N	/
203	C=NH	285.5457
204	>C=S	796.2358
205	aC-CON	652.2969
206	aC=O	224.6934
207	aN-	/
208	-Na	/
209	-K	/
210	HCONH	441.3234
211	CHOCH	/
212	C2O	/
213	SiH3	/
214	SiH2O	/
215	CH=C=CH	/
216	CH=C=C	/
217	OP(=S)O	/
218	R	/
219	CF2cyc	/
220	CFcyc	/

Table B. 2 Second-order group and their results of heat of combustion regression

n°	Group	D_j	n°	Group	D_j
1	(CH3)2CH	-0.561	66	aC-CH(CH3)2	/
2	(CH3)3C	-3.6436	67	aC-C(CH3)3	1.1631
3	CH(CH3)CH(CH3)	9.7135	68	aC-CF3	/
4	CH(CH3)C(CH3)2	10.9799	69	(CHn=C)(cyc)-CHO (n in 0..2)	/
5	C(CH3)2C(CH3)2	4.6363	70	(CHn=C)cyc-COO-CHm (n,m in 0..3)	/
6	CHn=CHm-CHp=CHk (k,m,n,p in 0..2)	-8.4061	71	(CHn=C)cyc-CO- (n in 0..2)	38.4116
7	CH3-CHm=CHn (m,n in 0..2)	3.4946	72	(CHn=C)cyc-CH3 (n in 0..2)	-20.1945
8	CH2-CHm=CHn (m,n in 0..2)	3.1731	73	(CHn=C)cyc-CH2 (n in 0..2)	/
9	CHp-CHm=CHn (m,n in 0..2; p in 0..1)	7.6974	74	(CHn=C)cyc-CN (n in 0..2)	/
10	CHCHO or CCHO	5.8991	75	(CHn=C)cyc-Cl (n in 0..2)	/
11	CH3COCH2	-10.0453	76	CHcyc-CH3	-0.3501
12	CH3COCH or CH3COC	/	77	CHcyc-CH2	17.3266
13	CHCOOH or CCOOH	22.9853	78	CHcyc-CH	-35.8871
14	CH3COOCH or CH3COOC	9.9917	79	CHcyc-C	12.0499
15	CO-O-CO	/	80	CHcyc-CH=CHn (n in 1..2)	/
16	CHOH	-0.7186	81	CHcyc-C=CHn (n in 1..2)	30.7484
17	COH	4.8725	82	CHcyc-Cl	/
18	CH3COCHnOH (n in 0..2)	/	83	CHcyc-F	/
19	NCCHOH or NCCOH	/	84	CHcyc-OH	7.9943
20	OH-CHn-COO (n in 0..2)	29.1071	85	CHcyc-NH2	/
21	CHm(OH)CHn(OH) (m,n in 0..2)	2.0551	86	CHcyc-NH-CHn (n in 0..3)	4.7813
22	CHm(OH)CHn(NHp) (m,n,p in 0..2)	/	87	CHcyc-N-CHn (n in 0..3)	/
23	CHm(NH2)CHn(NH2) (m,n in 0..2)	18.3727	88	CHcyc-SH	/
24	CHm(NH)CHn(NH2) (m,n in 1..2)	/	89	CHcyc-CN	7.3828
25	H2NCOCHnCHmCONH2 (m,n in 1..2)	-23.1852	90	CHcyc-COOH	/
26	CHm(NHn)-COOH (m,n in 0..2)	9.3951	91	CHcyc-CO	-7.5247
27	HOOC-CHn-COOH (n in 1..2)	/	92	CHcyc-NO2	/
28	HOOC-CHn-CHm-COOH (n, m in 1..2)	/	93	CHcyc-S-	/
29	HO-CHn-COOH (n in 1..2)	/	94	CHcyc-CHO	/
30	NH2-CHn-CHm-COOH (n, m in 1..2)	/	95	CHcyc-O-	-4.4766
31	CH3-O-CHn-COOH (n in 1..2)	/	96	CHcyc-OOCH	/
32	HS-CH-COOH	/	97	CHcyc-COO	/
33	HS-CHn-CHm-COOH (n, m in 1..2)	/	98	CHcyc-OOC	/
34	NC-CHn-CHm-CN (n, m in 1..2)	/	99	Ccyc-CH3	-0.227
35	OH-CHn-CHm-CN (n, m in 1..2)	/	100	Ccyc-CH2	-3.704
36	HS-CHn-CHm-SH (n, m in 1..2)	/	101	Ccyc-OH	-46.286
37	COO-CHn-CHm-OOC (n, m in 1..2)	/	102	>Ncyc-CH3	2.7032
38	OOC-CHm-CHm-COO (n, m in 1..2)	-33.1292	103	>Ncyc-CH2	/
39	NC-CHn-COO (n in 1..2)	-1.034	104	AROMRINGs1s2	-5.5183
40	COCHnCOO (n in 1..2)	38.9847	105	AROMRINGs1s3	-4.9474

41	CHm-O-CHn=CHp (m,n,p in 0..3)	-11.9384	106	AROMRINGs1s4	-7.8874
42	CHm=CHn-F (m,n in 0..2)	/	107	AROMRINGs1s2s3	15.9083
43	CHm=CHn-Br (m,n in 0..2)	/	108	AROMRINGs1s2s4	45.2034
44	CHm=CHn-I (m,n in 0..2)	/	109	AROMRINGs1s3s5	-100
45	CHm=CHn-Cl (m,n in 0..2)	/	110	AROMRINGs1s2s3s4	/
46	CHm=CHn-CN (m,n in 0..2)	-6.6045	111	AROMRINGs1s2s3s5	9.6422
47	CHn=CHm-COO-CHp (m,n,p in 0..3)	-14.5688	112	AROMRINGs1s2s4s5	/
48	CHm=CHn-CHO (m,n in 0..2)	-9.3178	113	PYRIDINEs2	/
49	CHm=CHn-COOH (m,n in 0..2)	/	114	PYRIDINEs3	/
50	aC-CHn-X (n in 1..2) X: Halogen	/	115	PYRIDINEs4	/
51	aC-CHn-NHm (n in 1..2; m in 0..2))	/	116	PYRIDINEs2s3	/
52	aC-CHn-O- (n in 1..2)	35.888	117	PYRIDINEs2s4	/
53	aC-CHn-OH (n in 1..2)	-100	118	PYRIDINEs2s5	/
54	aC-CHn-CN (n in 1..2)	/	119	PYRIDINEs2s6	/
55	aC-CHn-CHO (n in 1..2)	/	120	PYRIDINEs3s4	/
56	aC-CHn-SH (n in 1..2)	/	121	PYRIDINEs3s5	/
57	aC-CHn-COOH (n in 1..2)	/	122	PYRIDINEs2s3s6	/
58	aC-CHn-CO- (n in 1..2)	/	123	(CHn=CHm)cyc-COOH	/
59	aC-CHn-S- (n in 1..2)	/	124	AROMRINGs1s2s3s4s5	27.5814
60	aC-CHn-OOC-H (n in 1..2)	/	125	aC-NHCOCH2N	/
61	aC-CHm-NO2 (n in 1..2)	/	126	(N=C)cyc-CH3	/
62	aC-CHn-CONH2 (n in 1..2)	/	127	aC-CONH(CH2)2N	/
63	aC-CHn-OOC (n in 1..2)	/	128	aC-SO2NHn (n>=0;n<3)	/
64	aC-CHn-COO (n in 1..2)	/	129	aC-SO2NHn (n>=0;n<3)	/
65	aC-SO2-OH	/	130	aC-SO2NHn (n>=0;n<3)	/

Table B. 3 Third-order group and their results of heat of combustion regression

n^0	Group	E_k
1	HOOC-(CHn)m-COOH (m>2, n in 0..2)	-11.2018
2	NHn-(CHn)m-COOH (m>2, n in 0..2)	/
3	NH2-(CHn)m-OH (m>2, n in 0..2)	/
4	OH-(CHn)m-OH (m>2, n in 0..2)	18.7254
5	OH-(CHp)k-O-(CHn)m-OH (m,k>0; p,n in 0..2)	/
6	OH-(CHp)k-S-(CHn)m-OH (m,k>0; p,n in 0..2)	/
7	OH-(CHp)k-NHx-(CHn)m-OH (m,k>0; p,n,x in 0..2)	/
8	CHp-O-(CHn)m-OH (m>2; n,p in 0..2)	/
9	NH2-(CHn)m-NH2 (m>2; n in 0..2))	/
10	NHk-(CHn)m-NH2 (m>2; k in 0..1; n in 0..2)	/
11	SH-(CHn)m-SH (m>2; n in 0..2)	/
12	NC-(CHn)m-CN (m>2)	/
13	COO-(CHn)m-OOC (m>2; n in 0..2)	/
14	aC-(CHn=CHm)cyc (fused rings) (n,m in 0..1)	/
15	aC-aC (different rings)	2.0124
16	aC-CHncyc (different rings) (n in 0..1)	0
17	aC-CHncyc (fused rings) (n in 0..1)	-27.7726
18	aC-(CHn)m-aC (different rings) (m>1; n in 0..2)	-2.9371
19	aC-(CHn)m-CHcyc (different rings) (m>0; n in 0..2)	0
20	CHcyc-CHcyc (different rings)	21.6695
21	CHcyc-(CHn)m-CHcyc (different rings) (m>0; n in 0..2)	56.3033
22	CH multiring	-41.3318
23	C multiring	62.2134
24	aC-CHm-aC (different rings) (m in 0..2)	-33.433
25	aC-(CHm=CHn)-aC (different rings) (m,n in 0..2)	-27.9056
26	(CHm=C)cyc-CH=CH-(C=CHn)cyc (different rings)	/
27	(CHm=C)cyc-CHp-(C=CHn)cyc (different rings)	/
28	aC-CO-aC (different rings)	/
29	aC-CHm-CO-aC (different rings) (m in 0..2)	/
30	aC-CO-(C=CHn)cyc (different rings) (n in 0..1)	/
31	aC-CO-CO-aC (different rings)	/
32	aC-COcyc (fused rings)	-18.0795
33	aC-CO-(CHn)m-CO-aC (different rings) (m>0; n in 0..2)	/
34	aC-CO-CHncyc (different rings) (n in 0..1)	/
35	aC-CO-NHn-aC (different rings) (n in 0..1)	2.3916
36	aC-NHnCONHm-aC (different rings) (n,m in 0..1)	/
37	aC-CO-Ncyc (different rings)	/
38	aC-Scyc (fused rings)	/
39	aC-S-aC (different rings)	/
40	aC-POn-aC (different rings) (n in 0..4)	/
41	aC-SOn-aC (different rings) (n in 1..4)	/
42	aC-NHncyc (fused rings) (n in 0..1)	13.631
43	aC-NH-aC (different rings)	-0.2413
44	aC-(C=N)cyc (different rings)	/

45	aC-(N=CHn)cyc (fused rings) (n in 0..1)	13.631
46	aC-(CHn=N)cyc (fused rings) (n in 0..1)	/
47	aC-O-CHn-aC (different rings) (n in 0..2)	/
48	aC-O-aC (different rings)	/
49	aC-CHn-O-CHm-aC (different rings) (n,m in 0..2)	/
50	aC-Ocyc (fused rings)	/
51	AROM.FUSED[2]	31.8471
52	AROM.FUSED[2]s1	-12.2191
53	AROM.FUSED[2]s2	-0.895
54	AROM.FUSED[2]s2s3	/
55	AROM.FUSED[2]s1s4	-18.1096
56	AROM.FUSED[2]s1s2	/
57	AROM.FUSED[2]s1s3	/
58	AROM.FUSED[3]	/
59	AROM.FUSED[4a]	/
60	AROM.FUSED[4a]s1	/
61	AROM.FUSED[4a]s1s4	/
62	AROM.FUSED[4p]	/
63	AROM.FUSED[4p]s3s4	/
64	PYRIDINE.FUSED[2]	-11.0943
65	PYRIDINE.FUSED[2-iso]	/
66	PYRIDINE.FUSED[4]	/
67	aC-N-CHcyc (different rings)	/
68	N multiring	/
69	Ncyc-(CH2)3-Ncyc (different rings)	/
70	aC-COCH2CH2-aC (different rings)	/
71	aC-O-(CH2)2-Ncyc (different rings)	/
72	aC-CH(OH)(CH2)2-CHcyc (different rings)	/
73	Ncyc-(CH2)2-CHcyc (different rings)	/
74	aC-CONHCH2-CHcyc (different rings)	/

Appendix C

Data point for testing the GC method

Table C. 1 Data point used to validate the GC of heat of combustion

n°	Chemicals	Cas Number	Hcexp (KJ/mol)	Hc est. (KJ/mol)	RD%
1	Cyclopropane	000075-19-4	2091.4	2056.3	1.68
2	1-Hexanol, 2-ethyl-	000104-76-7	5287.8	5279.6	0.15
3	1-Propanamine	000107-10-8	2354.5	2355.0	0.02
4	Pentane	000109-66-0	3509.2	3526.4	0.49
5	1-Hexanol	000111-27-3	3980.8	3988.1	0.18
6	Tetradecanoic acid, methyl ester	000124-10-7	9438.2	9419.6	0.20
7	Hexanoic acid	000142-62-1	3492.4	3498.2	0.17
8	Decanoic acid	000334-48-5	6079.3	6109.6	0.50
9	2-Methylheptane	000592-27-8	5456.3	5470.2	0.26
10	Benzene, octyl-	002189-60-8	8474.2	8484.4	0.12
11	2-Cyclopropylhexane	006976-28-9	5648.0	5896.6	4.40
12	1,2-Ethanediamine	000107-15-3	1867.3	1854.9	0.67
13	Propanoic acid, ethyl ester	000105-37-3	2898.0	2891.2	0.24
14	Butanoic acid, 2-methyl-	000116-53-0	2842.2	2854.2	0.42
15	Ethane, 1,1'-oxybis 2-methoxy-	000111-96-6	3805.5	3773.8	0.83
16	Undecanoic acid	000112-37-8	6736.5	6762.4	0.39
17	Benzene, pentamethyl-	000700-12-9	6480.1	6211.8	4.14
18	Heptane, 1,1-dicyclohexyl-	002090-15-5	12030.5	12100.4	0.58
19	Benzene, 3-butenyl-	000768-56-9	5683.5	5702.7	0.34
20	3-Butynylbenzene	016520-62-0	5612.8	5609.9	0.05
21	1-Hexanol, 3,5,5-trimethyl-	003452-97-9	5943.0	5916.8	0.44
22	2-Propenoic acid	000079-10-7	1371.9	1366.2	0.42
23	Ethyl 2-cyanopropanoate	001572-99-2	3276.8	3264.2	0.38
24	Acetamide,ethoxy	51770-98-0	2369.4	2372.6	0.13
25	Ethyl ethoxymethyl ketone	076086-05-0	3636.1	3615.9	0.56
26	Acetic acid, ethoxy-, ethyl ester	000817-95-8	3436.5	3400.1	1.06
27	Acetic acid, ethoxy-	000627-03-2	2069.0	2048.7	0.98
28	Benzenepropanenitrile, β-oxo-	000614-16-4	4549.7	4510.1	0.87
29	Phenylpropargyl aldehyde	002579-22-8	4527.9	4546.4	0.41
30	1-Butene, 2,3,3-trimethyl-	000594-56-9	4637.7	4648.3	0.23
31	Pentene, 4,4-dimethyl-, (Z)-	000762-63-0	4650.1	4645.1	0.11
32	Ethyl 2-cyanoacetoacetate	000634-55-9	3504.0	3533.5	0.84
33	Acetylacetone	000123-54-6	2655.3	2661.3	0.22
34	4-Octanone	000589-63-9	5048.6	5065.4	0.33
35	Cyclohexanol, 2-methyl-, cis-	007443-70-1	4371.1	4382.0	0.25
36	Ethyl acetoacetate	000141-97-9	3160.3	3150.4	0.31
37	2-Pentanone, 4-hydroxy-4-methyl-	000123-42-2	3483.3	3548.4	1.87
38	Ethyl diacetoacetate	000603-69-0	4073.5	4092.8	0.47

39	Acetic acid, cyano-	000372-09-8	1254.0	1245.8	0.65
40	3-Buten-2-one, 4-phenyl-	000122-57-6	5282.3	4995.6	5.43
41	Benzeneacetonitrile, α-oxo-	000613-90-1	3918.8	3868.3	1.29
42	Pentane, 2,3-dimethyl-	000565-59-3	4807.9	4813.0	0.11
43	Benzenamine, N-ethyl-	000103-69-5	4724.2	4692.6	0.67
44	Benzene, 2-propenyl-	000300-57-2	5169.3	5049.9	2.31
45	trans-1-Phenyl-1-propene (á-methyl styrene)	000873-66-5	4985.2	4768.8	4.34
46	Propanoic acid, ethyl ester	000105-37-3	2898.0	2891.2	0.24
47	3-Pyridinecarbonitrile	000100-54-9	3132.3	3179.6	1.51
48	Benzene, 1,4-diisocyanato-	000104-49-4	3696.0	3595.9	2.71
49	2-Nitroethanol	000625-48-9	1094.1	1177.3	7.60
50	Methane, trinitro-	000517-25-9	481.4	512.9	6.54
51	1-Propanol, 2-methyl-2-nitro-	000076-39-1	2450.1	2421.4	1.17

Appendix D

Chemical databases

Table D. 1 List of chemicals for gasoline blend problem 1.2

n°	Compounds	Formula	CAS Number
1	Propane	C3H8	000074-98-6
2	n-butane	C4H10	000106-97-8
3	Isobutane	C4H10	000075-28-5
4	n-pentane	C5H12	000109-66-0
5	2-methylbutane	C5H12	000078-78-4
6	2,2-dimethylpropane	C5H12	000463-82-1
7	n-hexane	C6H14	000110-54-3
8	2-methylpentane	C6H14	000107-83-5
9	3-methylpentane	C6H14	000096-14-0
10	3-methylhexane	C7H16	000589-34-4
11	3-ethylpentane	C7H16	000617-78-7
12	2,2-dimethylpentane	C7H16	000590-35-2
13	2,4-dimethylpentane	C7H16	000108-08-7
14	3,3-dimethylpentane	C7H16	000562-49-2
15	2,2,3-trimethylbutane	C7H16	000464-06-2
16	2-methylheptane	C8H18	000592-27-8
17	3-methylheptane	C8H18	000589-81-1
18	2,2-dimethylhexane	C8H18	000590-73-8
19	2,3-dimethylhexane	C8H18	000584-94-1
20	2,4-dimethylhexane	C8H18	000589-43-5
21	2,5-dimethylhexane	C8H18	000592-13-2
22	3,4-dimethylhexane	C8H18	000583-48-2
23	2-methyl-3-ethylpentane	C8H18	000609-26-7
24	3-methyl-3-ethylpentane	C8H18	001067-08-9
25	2,2,3-trimethylpentane	C8H18	000564-02-3
26	2,3,4-trimethylpentane	C8H18	000565-75-3
27	Decane	C10H22	000124-18-5
28	Hexadecane	C16H34	000544-76-3
29	Cyclopropane	C3H6	000075-19-4
30	Cyclobutane	C4H8	000287-23-0
31	Methylcyclopropane	C4H8	000594-11-6

32	Cyclopentane	C5H10	000287-92-3
33	1,1-dimethylcyclopropane	C5H10	001630-94-0
34	Cyclohexane	C6H12	000110-82-7
35	Methylcyclopentane	C6H12	000096-37-7
36	Isopropylcyclopropane	C6H12	003638-35-5
37	1,1,2-trimethylcyclopropane	C6H12	004127-45-1
38	1-ethyl-1-methylcyclopropane	C6H12	053778-43-1
39	Cycloheptane	C7H14	000291-64-5
40	Methylcyclohexane	C7H14	000108-87-2
41	1,1-dimethylcyclopentane	C7H14	001638-26-2
42	Trans-1,3-dimethylcyclopentane	C7H14	001759-58-6
43	Cis-1,3-dimethylcyclopentane	C7H14	002532-58-3
44	1-ethyl-1-methylcyclopentane	C8H16	016747-50-5
45	Trans-1,2-dimethylcyclohexane	C8H16	006876-23-9
46	1,1-dimethylcyclohexane	C8H16	000590-66-9
47	Trans-1,3-dimethylcyclohexane	C8H16	002207-03-6
48	1-methylethyl-cyclopentane	C8H16	003875-51-2
49	1,1'-bicyclohexyl	C12H22	000092-51-3
50	Methanol	CH4O	000067-56-1
51	Ethanol	C2H6O	000064-17-5
52	1,2-ethanediol	C2H6O2	000107-21-1
53	Isopropanol	C3H8O	000067-63-0
54	1-propanol	C3H8O	000071-23-8
55	1,2-propylene-glycol	C3H8O2	000057-55-6
56	1,3-propylene-glycol	C3H8O2	000504-63-2
57	1-butanol	C4H10O	000071-36-3
58	2-butanol	C4H10O	000078-92-2
59	2-methyl-1-propanol	C4H10O	000078-83-1
60	2-methyl-2-propanol	C4H10O	000075-65-0
61	1,2-butanediol	C4H10O2	000584-03-2
62	1,3-butanediol	C4H10O2	000107-88-0
63	1,4-butanediol	C4H10O2	000110-63-4
64	2,3-butanediol	C4H10O2	006982-25-8
65	1-pentanol	C5H12O	000071-41-0
66	2-pentanol	C5H12O	006032-29-7
67	3-pentanol	C5H12O	000584-02-1
68	2-methyl-1-butanol	C5H12O	000137-32-6
69	2-methyl-2-butanol	C5H12O	000075-85-4
70	3-methyl-1-butanol	C5H12O	000123-51-3
71	3-methyl-2-butanol	C5H12O	000598-75-4

72	2,2-dimethyl-1-propanol	C5H12O	000075-84-3
73	1,4-pentanediol	C5H12O2	000626-95-9
74	1,5-pentanediol	C5H12O2	000111-29-5
75	2,4-pentanediol	C5H12O2	000625-69-4
76	2-methylbutane-2,3-diol	C5H12O2	005396-58-7
77	1,3-propanediol, 2,2-dimethyl-	C5H12O2	000126-30-7
78	1-hexanol	C6H14O	000111-27-3
79	2-methyl-1-pentanol	C6H14O	000105-30-6
80	4-methyl-2-pentanol	C6H14O	000108-11-2
81	2-pentanol, 2-methyl-	C6H14O	000590-36-3
82	2-butanol, 3,3-dimethyl-	C6H14O	000464-07-3
83	1,5-hexanediol	C6H14O2	000928-40-5
84	1,6-hexanediol	C6H14O2	000629-11-8
85	2,3-hexanediol	C6H14O2	000617-30-1
86	2-methyl-2,4-pentandiol	C6H14O2	000107-41-5
87	3-methyl-2,4-pentanediol	C6H14O2	005683-44-3
88	1-heptanol	C7H16O	000111-70-6
89	2-methyl-2-hexanol	C7H16O	000625-23-0
90	3-methyl-2-hexanol	C7H16O	002313-65-7
91	2,3-dimethyl-3-pentanol	C7H16O	000595-41-5
92	3,4-dimethyl-2-pentanol	C7H16O	064502-86-9
93	2,3,3-trimethyl-2-butanol	C7H16O	000594-83-2
94	Cyclohexanol	C6H12O	000108-93-0
95	1-methylcyclohexanol	C7H14O	000590-67-0
96	Diethylene-glycol	C4H10O3	000111-46-6
97	2-methoxyethanol	C3H8O2	000109-86-4
98	1,2-epoxybutane	C4H8O	000106-88-7
99	Diethyl-ether	C4H10O	000060-29-7
100	1,2-dimethoxyethane	C4H10O2	000110-71-4
101	2-ethoxyethanol	C4H10O2	000110-80-5
102	Diisopropyl-ether	C6H14O	000108-20-3
103	2-butoxyethanol	C6H14O2	000111-76-2
104	2-(2-methoxyethoxy) ethanol	C5H12O3	000111-77-3
105	2-(2-ethoxyethoxy) ethanol	C6H14O3	000111-90-0
106	Ethane, 1,1'-oxybis[2-methoxy-	C6H14O3	000111-96-6
107	Dimethyl-ether	C2H6O	000115-10-6
108	Ethane, methoxy-	C3H8O	000540-67-0
109	Methyl-n-propyl-ether	C4H10O	000557-17-5
110	Methyl-isopropyl-ether	C4H10O	000598-53-8
111	Methyl-isobutyl-ether	C5H12O	000625-44-5

112	Ethyl-isopropyl-ether	C5H12O	000625-54-7
113	Butane, 1-methoxy-	C5H12O	000628-28-4
114	Ethyl-propyl-ether	C5H12O	000628-32-0
115	1,2-diethoxyethane	C6H14O2	000629-14-1
116	Propane, 2-ethoxy-2-methyl-	C6H14O	000637-92-3
117	Ethyl-tert-pentyl-ether	C7H16O	000919-94-8
118	Methyl-tert-pentyl-ether	C6H14O	000994-05-8
119	Methyl-tert-butyl-ether	C5H12O	001634-04-4
120	Methyl-sec-butyl-ether	C5H12O	006795-87-5
121	Ethylal	C5H12O2	000462-95-3
122	1-hexanal	C6H12O	000066-25-1
123	Acetaldehyde	C2H4O	000075-07-0
124	2-methylpropanal	C4H8O	000078-84-2
125	Acetal	C6H14O2	000105-57-7
126	1-pentanal	C5H10O	000110-62-3
127	1-heptanal	C7H14O	000111-71-7
128	1-propanal	C3H6O	000123-38-6
129	Butanal	C4H8O	000123-72-8
130	Octanal	C8H16O	000124-13-0
131	3-methylhexanal	C7H14O	019269-28-4
132	3-hydroxy-2-methyl-propionaldehyde	C4H8O2	038433-80-6
133	3-pentanone, 2,2-dimethyl-	C7H14O	000564-04-5
134	Acetone	C3H6O	000067-64-1
135	2-butanone, 3,3-dimethyl-	C6H12O	000075-97-8
136	2-butanone	C4H8O	000078-93-3
137	3-pentanone	C5H10O	000096-22-0
138	2-pentanone	C5H10O	000107-87-9
139	Diisobutyl-ketone	C9H18O	000108-83-8
140	Cyclohexanone	C6H10O	000108-94-1
141	5-methyl-2-hexanone	C7H14O	000110-12-3
142	2-heptanone	C7H14O	000110-43-0
143	2-octanone	C8H16O	000111-13-7
144	Cyclopentanone	C5H8O	000120-92-3
145	4-heptanone	C7H14O	000123-19-3
146	Acetylacetone	C5H8O2	000123-54-6
147	Methyl-isopropyl-ketone	C5H10O	000563-80-4
148	3-methyl-2-pentanone	C6H12O	000565-61-7
149	Ethyl-isopropyl-ketone	C6H12O	000565-69-5
150	3-hexanone	C6H12O	000589-38-8
151	2-hexanone	C6H12O	000591-78-6

152	2-nonanone	C9H18O	000821-55-6
153	2-propanone, 1-hydroxy-	C3H6O2	000116-09-6
154	Propylene-glycol-monomethyl-ether-acetate	$C_6H_{12}O_3$	000108-65-6
155	Methyl-acetate	C3H6O2	000079-20-9
156	Isobutyl-isobutyrate	C8H16O2	000097-85-8
157	Methyl-acetoacetate	C5H8O3	000105-45-3
158	Acetic acid, 1-methylpropyl ester	C6H12O2	000105-46-4
159	Acetic acid, anhydride	C4H6O3	000108-24-7
160	Propylene glycol me ether acetate	C6H12O3	000108-65-6
161	n-propyl-acetate	C5H10O2	000109-60-4
162	Formic acid, ethyl ester	C3H6O2	000109-94-4
163	2-ethoxyethyl-acetate	C8H12O3	000111-15-9
164	Ethylene-glycol-diacetate	C6H10O4	000111-55-7
165	Acetic acid, butyl ester	C6H12O2	000123-86-4
166	Ethyl-acetate	C4H8O2	000141-78-6
167	Acetic acid, hexyl ester	C8H16O2	000142-92-7
168	2-oxepanone	C6H10O2	000502-44-3
169	Acetic acid, 1,1-dimethylethyl ester	C6H12O2	000540-88-5
170	Formic acid, 2-methylpropyl ester	C5H10O2	000542-55-2
171	Propanoic acid, 2-methyl-, methyl ester	C5H10O2	000547-63-7
172	Methyl-propionate	C4H8O2	000554-12-1
173	Cyclohexyl-acetate	C8H14O2	000622-45-7
174	Methyl-n-butyrate	C5H10O2	000623-42-7
175	1-butanol, 2-methyl-, acetate	C7H14O2	000624-41-9
176	2-methylbutan-2-yl acetate	C7H14O2	000625-16-1
177	Ethyl-3-ethoxypropionate	C7H14O3	000763-69-9
178	Acetic acid	C2H4O2	000064-19-7
179	Neopentanoic-acid	C5H10O2	000075-98-9
180	Propionic-acid	C3H8O2	000079-09-4
181	Isobutyric-acid	C4H8O2	000079-31-2
182	2-ethyl-butyric-acid	C6H12O2	000088-09-5
183	Diethyl-oxalate	C6H10O4	000095-92-1
184	n-butyric-acid	C4H8O2	000107-92-6
185	n-pentanoic-acid	C5H10O2	000109-52-4
186	Heptanoic acid	C7H14O2	000111-14-8
187	Hexanoic acid	C6H12O2	000142-62-1
188	2-methylbutyric-acid	C5H10O2	000600-07-7
189	Ethylamine	C2H7N	000075-04-7
190	Trimethylamine	C3H9N	000075-50-3
191	1-propanamine, 2-methyl-	C4H11N	000078-81-9

192	1-amino-2-propanol	C3H9NO	000078-96-6
193	N-methylcyclohexylamine	C7H15N	000100-60-7
194	Methyl-diethanolamine	C5H13NO2	000105-59-9
195	n-propylamine	C3H9N	000107-10-8
196	Ethylenediamine	C2H8N2	000107-15-3
197	1-butanamine	C4H11N	000109-73-9
198	Methylethanolamine	C3H9NO	000109-83-1
199	1-pentanamine	C5H13N	000110-58-7
200	Piperidine	C5H11N	000110-89-4
201	n-hexylamine	C6H15N	000111-26-2
202	Diethylene-triamine	C4H13N3	000111-40-0
203	Hexamethyleneimine	C6H13N	000111-49-9
204	n-heptylamine	C7H17N	000111-68-2
205	1-octanamine	C8H19N	000111-86-4
206	Triethylene-tetramine	C6H18N4	000112-24-3
207	Pyrrolidine, 1-methyl-	C5H11N	000120-94-5
208	Triethylamine	C6H15N	000121-44-8
209	Pyrrolidine	C4H9N	000123-75-1
210	Hexamethylenediamine	C6H16N2	000124-09-4
211	Dimethylamine	C2H7N	000124-40-3
212	Monoethanolamine	C2H7NO	000141-43-5
213	1-propanamine, n-propyl-	C6H15N	000142-84-7
214	Ethylenimine	C2H5N	000151-56-4
215	1-propanol, 3-amino-	C3H9NO	000156-87-6
216	2-aminoethoxyethanol	C4H11NO2	000929-06-6
217	Furan, tetrahydro-	C4H8O	000109-99-9
218	Tetrahydrofurfuryl alcohol	C5H10O2	000097-99-4
219	Furan, tetrahydro-2-methyl-	C5H10O	000096-47-9
220	Furan, tetrahydro-3-methyl-	C5H10O	013423-15-9
221	2(3h)-furanone, dihydro-5-methyl-	C5 H8 O2	000108-29-2

Table D. 2 List of chemicals for the lubricant problem 2.3

Group	Name	Formula	MW (g/mol)	Viscosity, (cSt 100C)	Melting Point (K)
Paraffin	Undecane	C11H24	156.31	0.640	247.55
	Octadecane	C18H38	254.49	1.558	301.35
	n-Nonadecane	C19H40	268.53	1.794	305.25
	n-Eicosane	C20H42	282.55	1.989	309.95
	n-Heneicosane	C21H44	296.58	2.071	313.65

	n-Tetracosane	C24H50	338.66	2.744	327.15
	n-Hexacosane	C26H54	366.72	3.240	329.55
	2-Methylpentadecane	C16H34	226.44	1.236	240.74
	4,9-Di-n-Propyldodecane	C18H38	254.49	1.234	249.41
	3-Methyleicosane	C21H44	296.57	2.114	275.25
	10-Methyleicosane	C21H44	296.57	1.974	275.25
	8-n-Hexylpentadecane	C21H44	296.57	1.761	275.25
Isoparaffin	2-Methyltricosane	C24H50	338.65	2.806	293.84
	11-butyldocosane	C26H54	366.71	2.733	303.80
	9-n-Butyldocosane	C26H54	366.70	2.768	303.80
	7-n-Butyldocosane	C26H54	366.70	2.871	303.80
	5-n-Butyldocosane	C26H54	366.70	2.970	303.80
	5,14-Di-n-Butyloctadecane	C26H54	366.70	2.780	299.89
	7-n-Hexyleicosane	C26H54	366.70	2.795	303.80
	3-Ethyltetracosane	C26H54	366.70	3.225	303.80
	Naphthalene, decahydro-	C10H18	138.25	1.083	230.15
	Dodecahydrofluorene	C13H22	178.31	1.638	268.82
	Phenanthrene, tetradecahydro-	C14H24	192.34	1.750	279.59
Napthenes	Fluoranthene, hexadecahydro-	C16H26	218.38	2.510	298.22
	Chrysene, octadecahydro-	C18H30	246.43	3.980	388.15
	1H-Dibenzo[a,i]fluorene, eicosahydro-	C21H34	286.49	10.660	337.23
	2-Octylperhydrotriphenylene	C26H46	358.64	8.670	347.70
	2-Decylperhydroindeno[2,. 1-a]indene.	C26H46	358.64	6.020	342.31
	1,1'-Biphenyl	C12H10	154.21	0.988	342.15
	1-Phenyloctane	C14H22	190.32	0.946	237.15
	2-n-Butyl Naphthalene	C14H16	184.28	1.137	268.15
Aromatic	1-Phenyl Decane	C16H26	218.38	1.220	258.75
	7-Phenyltridecane	C19H32	260.46	1.649	279.00
	2-Phenyleicosane	C26H46	358.64	3.330	302.15
	3-n-Decylpyrene	C26H30	342.52	7.091	439.05
Bio-based	propane-1,2,3-triol	C3H8O3	92.095	6.747	25.2193
	n-tetradecanoic-acid	C14H28O2	228.38	2.693	5.2439
	n-hexadecanoic-acid	C16H32O2	256.43	3.639	4.7883
	Octadecanoic acid	C18H36O2	284.483	4.338	4.3977
	9-Octadecenoic acid (Z)-	C18H34O2	282.467	3.503	4.5320
	9,12-Octadecadienoic acid (Z,Z)-	C18H32O2	280.451	2.936	4.6666
	Dodecanoic acid	C12H24O2	200.32	2.290	5.8200
	Ethanedioic acid, diethyl ester	C6H10O4	146.143	0.475	8.3649
	Carbonic acid, diethyl ester	C5H10O3	118.133	0.406	8.8945
	Butanoic acid, propyl ester	C7H14O2	130.187	0.399	7.2969

Table D. 3 List of chemicals for the lubricant problem 2.4

n°	Name	Formula	CAS num	Smile	MW (g/mol)	Tm/PP (K)	Viscosity (100C) cSt	Viscosity (40) cSt	Density (25) (g/cm3)
1	2,4-dimethylhexane	000589-43-5	C8H18	CC(C)CC(C)CC	114.23	144.30	0.4109	0.6891	0.6932
2	2,4-dimethyl-3-ethylpentane	001068-87-7	C9H20	CCC(C(C)C)C(C)C	128.26	150.75	0.4479	0.7897	0.7342
3	2,3-dimethylhexane	000584-94-1	C8H18	CC(C)C(C)CCC	114.23	152.00	0.3635	0.5709	0.7082
4	2,2-dimethylhexane	000590-73-8	C8H18	CC(C)(C)CCCC	114.23	152.05	0.3589	0.6007	0.6918
5	2,2,3,4-tetramethylpentane	001186-53-4	C9H20	CC(C)(C)C(C)C(C)C	128.26	152.15	0.4087	0.8139	0.7352
6	3-ethylhexane	000619-99-8	C8H18	C(CCC)(CC)CC	114.23	153.47	0.3242	0.5221	0.7096
7	Propylcyclopentane	002040-96-2	C8H16	CCCC1CCCC1	112.21	155.85	0.4585	0.7104	0.7729
8	2-methyl-3-ethylpentane	000609-26-7	C8H18	CC(C)C(CC)CC	114.23	158.25	0.3198	0.5171	0.7164
9	3-ethylheptane	015869-80-4	C9H20	CCCCC(CC)CC	128.26	158.25	0.3750	0.6309	0.7225
10	2,4,4-trimethylhexane	016747-30-1	C9H20	CCC(C)(C)CC(C)C	128.26	159.75	0.4078	0.8032	0.7201
11	4-methyloctane	002216-34-4	C9H20	CCCC(C)CCCC	128.26	159.85	0.3788	0.6368	0.7164
12	2,2-dimethylheptane	001071-26-7	C9H20	CCCCCC(C)(C)C	128.26	160.15	0.4677	0.8210	0.7066
13	2,2,3-trimethylpentane	000564-02-3	C8H18	CC(C)(C)C(C)CC	114.23	160.95	0.3952	0.6636	0.7124
14	Ethylcyclohexane	001678-91-7	C8H16	CCC1CCCCC1	112.21	161.85	0.5086	0.8423	0.7845
15	2,3,4-trimethylpentane	000565-75-3	C8H18	C(C(C(C)C)C)(C)C	114.23	163.95	0.4023	0.6668	0.7161
16	Cyclopentane, butyl-	002040-95-1	C9H18	C(CC1)CC1CCCC	126.24	165.15	0.5105	0.8890	0.7813
17	3-methyloctane	002216-33-3	C9H20	CCC(C)CCCCC	128.26	165.55	0.3789	0.6363	0.7167
18	2,2,4-trimethylpentane	000540-84-1	C8H18	C(CC(C)C)(C)(C)C	114.23	165.85	0.3711	0.5948	0.6904
19	2,2,5-trimethylhexane	003522-94-9	C9H20	CC(C)(C)CCC(C)C	128.26	167.45	0.2778	0.4273	0.7038
20	2,6-dimethylheptane	001072-05-5	C9H20	CC(C)CCCC(C)C	128.26	170.25	0.4676	0.8221	0.7058
21	2,3,3,4-tetramethylpentane	016747-38-9	C9H20	CC(C)C(C)(C)C(C)C	128.26	171.05	0.4095	0.8173	0.7511
22	2,4-Dimethyloctane	004032-94-4	C10H22	CC(CC(CCCC)C)C	142.28	172.73	0.5323	0.9690	0.7224
23	2,5-dimethyloctane	015869-89-3	C10H22	CCCC(C)CCC(C)C	142.28	172.73	0.5255	0.9620	0.7264
24	2,6-Dimethyloctane	002051-30-1	C10H22	CCC(C)CCCC(C)C	142.28	172.73	0.5298	0.9664	0.7236
25	Acetal	000105-57-7	C6H14O2	O(C(OCC)C)CC	118.18	173.15	0.2574	0.4366	0.8215
26	3-methylheptane	000589-81-1	C8H18	C(CCCC)(CC)C	114.23	173.15	0.3499	0.5632	0.7014
27	di-sec-butyl-ether	006863-58-7	C8H18O	O(C(CC)C)C(CC)C	130.23	173.15	0.4020	0.7116	0.7590
28	n-propylbenzene	000103-65-1	C9H12	c(cccc1)(c1)CCC	120.19	173.65	0.4498	0.7775	0.8595
29	2,2-dimethyl-3-ethylpentane	016747-32-3	C9H20	CCC(CC)C(C)(C)C	128.26	173.85	0.4497	0.7929	0.7311
30	4-Methylnonane(DL)	017301-94-9	C10H22	CCCCCC(C)CCC	142.28	174.15	0.4905	0.8598	0.7281

31	Isobutyl-acetate	000110-19-0	C6H12O2	O=C(OCC(C)C)C	116.16	174.35	0.3634	0.6494	0.8681
32	Ethyl-n-butyrate	000105-54-4	C6H12O2	O=C(OCC)CCC	116.16	175.15	0.3730	0.6091	0.8739
33	Cumene	000098-82-8	C9H12	c(cccc1)(c1)C(C)C	120.19	177.15	0.4185	0.7308	0.8594
34	m-ethyltoluene	000620-14-4	C9H12	CCc1cccc(C)c1	120.19	177.65	0.7375	1.5939	1.1747
35	DI-n-butyl-ether	000142-96-1	C8H18O	O(CCCC)CCCC	130.23	177.95	0.4046	0.7000	0.7641
36	n-propyl-n-butyrate	000105-66-8	C7H14O2	O=C(OCCC)CCC	130.19	177.95	0.4312	0.7647	0.8681
37	Ethylbenzene	000100-41-4	C8H10	c(cccc1)(c1)CC	106.17	178.25	0.3942	0.6397	0.8648
38	Cyclohexane, propyl-	001678-92-8	C9H18	CCCC1CCCCC1	126.24	178.25	0.5717	0.9750	0.7902
39	2,3-dimethyloctane	007146-60-3	C10H22	CCCCCC(C)C(C)C	142.28	179.63	0.5193	0.9523	0.7341
40	Tripropylamine	000102-69-2	C9H21N	N(CCC)(CCC)CCC	143.27	179.65	3.3186	18.6535	1.1191
41	n-propyl-acetate	000109-60-4	C5H10O2	O=C(OCCC)C	102.13	180.15	0.3151	0.5398	0.8822
42	n-butyl-formate	000592-84-7	C5H10O2	O=COCCCC	102.13	181.65	0.3615	0.6100	0.8869
43	2,5-dimethylhexane	000592-13-2	C8H18	CC(C)CCC(C)C	114.23	182.15	0.3680	0.5709	0.6900
44	3-methyl-3-ethylpentane	001067-08-9	C8H18	CCC(C)(CC)CC	114.23	182.25	0.3740	0.6173	0.7237
45	4-methyl-2-pentanol	000108-11-2	C6H14O	OC(CC(C)C)C	102.18	183.15	0.6855	2.8883	0.8034
46	Ethyl-isobutyrate	000097-62-1	C6H12O2	O=C(OCC)C(C)C	116.6	184.95	0.3233	0.5524	0.8662
47	n-butylbenzene	000104-51-8	C10H14	c(cccc1)(c1)CCCC	134.22	185.25	0.5143	0.9223	0.8577
48	5-methylnonane	015869-85-9	C10H22	CCCCC(C)CCCC	142.28	185.45	0.4994	0.8759	0.7285
49	cis-1,4-dimethylcyclohexane	000624-29-3	C8H16	C(CC(C1)C)C(C1)C	112.21	186.15	0.4999	0.8585	0.7787
50	Methyl-n-butyrate	000623-42-7	C5H10O2	O=C(OC)CCC	102.13	187.35	0.3218	0.5045	0.9380
51	5-ethyl-m-xylene	000934-74-7	C10H14	c(cc(cc1C)CC)(c1)C	134.22	188.85	0.4815	0.9806	0.8608
52	Methyl-isobutyl-ketone	000108-10-1	C6H12O	O=C(CC(C)C)C	100.16	189.15	0.3404	0.5755	0.7962
53	m-diethylbenzene	000141-93-5	C10H14	c(cccc1CC)(c1)CC	134.22	189.25	0.5144	0.9484	0.8600
54	1-methyl-3-n-propylbenzene	001074-43-7	C10H14	c(cccc1C)(c1)CCC	134.22	189.65	0.4969	0.9694	0.8570
55	n-hexyl-acetate	000142-92-7	C8H16O2	O=C(OCCCCCC)C	144.21	192.25	0.5050	0.9872	0.8682
56	o-ethyltoluene	000611-14-3	C9H12	c(c(ccc1)C)(c1)CC	120.19	192.35	0.4151	0.8098	0.8766
57	Isobutyl-isobutyrate	000097-85-8	C8H16O2	O=C(OCC(C)C)C(C)C	144.21	192.45	0.4297	0.8204	0.8494
58	2-methyloctane	003221-61-2	C9H20	CC(C)CCCCCC	128.26	192.85	0.4296	0.7209	0.7096
59	Isopentyl-acetate	000123-92-2	C7H14O2	O=C(OCCC(C)C)C	130.19	194.65	0.4392	0.7955	0.8666
60	n-butyl-acetate	000123-86-4	C6H12O2	O=C(OCCCC)C	116.16	195.15	0.3840	0.6514	0.8761
61	Glyceryl-triacetate	000102-76-1	C9H14O6	O=C(OCC(OC(=O)C)COC(=O)C)C	218.21	195.15	0.8098	2.1791	1.1548
62	n-propyl-propionate	000106-36-5	C6H12O2	O=C(OCCC)CC	116.16	197.25	0.3586	0.6117	0.8769
63	cis-1,3-dimethylcyclohexane	000638-04-0	C8H16	CC1CCCC(C)C1	112.21	197.55	0.5093	0.8687	0.7619

64	n-butyl-methacrylate	000097-88-1	C8H14O2	O=C(OCCCC)C(=C)C	142.2	198.15	0.3740	0.8547	0.8906
65	Butyric-anhydride	000106-31-0	C8H14O3	O=C(OC(=O)CCC)CCC	158.2	198.15	0.6210	1.2191	0.9620
66	n-pentylbenzene	000538-68-1	C11H16	c(cccc1)(c1)CCCCC	148.25	198.15	0.6240	1.1461	0.8547
67	2-butoxyethanol	000111-76-2	C6H14O2	O(CCCC)CCO	118.18	198.35	0.6772	2.4658	0.8964
68	Cyclohexane, butyl-	001678-93-9	C10H20	C(CCCC1)(C1)CCCC	140.27	198.45	0.6828	1.2179	0.7957
69	2-methylnonane	000871-83-0	C10H22	CCCCCCCC(C)C	142.28	198.55	0.5356	0.9392	0.7229
70	2,2-dimethyloctane	015869-87-1	C10H22	CC(CCCCCC)(C)C	142.28	198.64	0.5289	0.9693	0.7208
71	1,2-diethoxyethane	000629-14-1	C6H14O2	O(CCOCC)CC	118.18	199.15	0.3777	0.6678	0.8391
72	5-methyl-2-hexanone	000110-12-3	C7H14O	O=C(CCC(C)C)C	114.19	199.15	0.3887	0.7057	0.8082
73	n-pentyl-formate	000638-49-3	C6H12O2	O=COCCCCC	116.16	199.65	0.4055	0.7021	0.8812
74	diisobutylamine	000110-96-3	C8H19N	N(CC(C)C)CC(C)C	129.25	199.65	0.4456	0.7984	0.7425
75	Acetic-anhydride	000108-24-7	C4H6O3	O=C(OC(=O)C)C	102.09	200.15	0.3841	0.6584	1.0751
76	o-cymene	000527-84-4	C10H14	c(c(ccc1)C)(c1)C(C)C	134.22	201.65	0.5936	0.9534	0.8728
77	n-pentyl-acetate	000628-63-7	C7H14O2	O=C(OCCCCC)C	130.19	202.35	0.4318	0.7856	0.8721
78	2-ethyl-1-hexanol	000104-76-7	C8H18O	OCC(CCCC)CC	130.23	203.15	1.3221	5.7480	0.8296
79	Diisopropyl-ketone	000565-80-0	C7H14O	O=C(C(C)C)C(C)C	114.19	204.15	0.3247	0.5803	0.9119
80	di-n-pentyl-ether	000693-65-2	C10H22O	O(CCCCC)CCCCC	158.28	204.15	0.4856	1.0051	0.7799
81	p-cymene	000099-87-6	C10H14	c(ccc(c1)C)(c1)C(C)C	134.22	204.25	0.4713	0.7778	0.8524
82	diethylene-glycol-dimethyl-ether	000111-96-6	C6H14O3	O(CCOC)CCOC	134.18	205.15	0.4622	0.8713	0.9390
83	4-ethyl-o-xylene	000934-80-5	C10H14	c(ccc(c1C)C)(c1)CC	134.22	206.25	0.5085	1.0329	0.8706
84	2,2,4,4-tetramethylpentane	001070-87-7	C9H20	CC(C)(C)CC(C)(C)C	128.26	206.65	0.3535	0.7837	0.7156
85	m-cymene	000535-77-3	C10H14	c(cccc1C(C)C)(c1)C	134.22	209.45	0.5093	0.7910	0.8571
86	1-methyl-4-n-propylbenzene	001074-55-1	C10H14	c(ccc(c1)C)(c1)CCC	134.22	209.55	0.5230	0.9559	0.8544
87	n-ethylaniline	000103-69-5	C8H11N	N(c(cccc1)c1)CC	121.18	209.65	0.6652	1.5896	0.9576
88	m-diisopropylbenzene	000099-62-7	C12H18	c(cccc1C(C)C)(c1)C(C)C	162.27	210.05	0.8138	1.6510	0.8524
89	di-n-propylamine	000142-84-7	C6H15N	N(CCC)CCC	101.19	210.15	0.3425	0.5844	0.7372
90	4-ethyl-m-xylene	000874-41-9	C10H14	c(ccc(c1C)CC)(c1)C	134.22	210.25	0.4945	0.9480	0.8723
91	n-hexyl-formate	000629-33-4	C7H14O2	O=COCCCCCC	130.19	210.55	0.4769	0.8872	0.8749
92	p-ethyltoluene	000622-96-8	C9H12	c(ccc(c1)C)(c1)CC	120.19	210.85	0.4147	0.6563	0.8570
93	Di-n-butylamine	000111-92-2	C8H19N	N(CCCC)CCCC	129.25	211.15	0.4948	0.9589	0.7571
94	2-ethoxyethyl-acetate	000111-15-9	C8H12O3	O=C(OCCOCC)C	132.16	211.45	0.4064	0.8166	0.9689
95	Isobutyl-acrylate	000106-63-8	C7H12O2	O=C(OCC(C)C)C=C	128.17	212.15	0.4110	0.7194	0.8848
96	n-hexylbenzene	001077-16-3	C12H18	c(cccc1)(c1)CCCCCC	162.27	212.15	0.7266	1.3942	0.8545

97	Diethylene-glycol-di-n-butyl-ether	000112-73-2	C12H26O3	O(CCOCCOCCCC)CCCC	218.34	213.15	0.8607	1.8738	0.8813
98	tert-butylbenzene	000098-06-6	C10H14	c(cccc1)(c1)C(C)(C)C	134.22	215.55	0.5038	0.9471	0.8626
99	N-methylaniline	000100-61-8	C7H9N	N(c(cccc1)c1)C	107.16	216.15	0.6334	1.4806	0.9823
100	n-octane	000111-65-9	C8H18	C(CCCCCC)C	114.23	216.35	0.3972	0.6227	0.6992
101	1-hexanal	000066-25-1	C6H12O	O=CCCCCC	100.16	217.15	0.4478	0.7054	0.8097
102	3-hexanone	000589-38-8	C6H12O	O=C(CCC)CC	100.16	217.65	0.3546	0.6000	0.8101
103	2-hexanone	000591-78-6	C6H12O	O=C(CCCC)C	100.16	217.65	0.3566	0.6077	0.8070
104	2,7-dimethyloctane	001072-16-8	C10H22	CC(C)CCCCC(C)C	142.28	218.25	0.4878	0.8927	0.7201
105	2-ethyl-p-xylene	001758-88-9	C10H14	c(ccc(c1CC)C)(c1)C	134.22	219.45	0.5077	1.0290	0.8732
106	Nonane	000111-84-2	C9H20	C(CCCCCCC)C	128.26	219.65	0.4659	0.7879	0.7143
107	3,3-dimethyl-2-butanone	000075-97-8	C6H12O	O=C(C(C)(C)C)C	100.16	220.65	0.4071	0.6873	0.8021
108	Isobutylbenzene	000538-93-2	C10H14	c(cccc1)(c1)CC(C)C	134.22	221.75	0.5117	0.9616	0.8491
109	Indane	000496-11-7	C9H10	c(c(ccc1)CC2)(c1)C2	118.18	221.75	0.6106	1.1289	0.9599
110	Benzyl-acetate	000140-11-4	C9H10O2	O=C(OCc(cccc1)c1)C	150.18	221.85	0.5898	1.4591	1.0451
111	n-heptyl-acetate	000112-06-1	C9H18O2	O=C(OCCCCCCC)C	158.24	222.95	0.6743	1.2596	0.8660
112	Diethyl-malonate	000105-53-3	C7H12O4	O=C(OCC)CC(=O)OCC	160.17	223.15	0.5762	1.3842	1.0499
113	3-ethyl-o-xylene	000933-98-2	C10H14	c(c(c(cc1)C)C)(c1)CC	134.22	223.65	0.4824	1.0420	0.8881
114	Propylene-carbonate	000108-32-7	C4H6O3	O=C(OCC1C)O1	102.09	224.35	0.7946	1.5688	1.1984
115	Methyl-methacrylate	000080-62-6	C5H8O2	O=C(OC)C(=C)C	100.12	225.15	0.2983	0.4763	0.8837
116	n-heptylbenzene	001078-71-3	C13H20	c(cccc1)(c1)CCCCCCC	176.3	225.15	0.8462	1.6927	0.8541
117	m-xylene	000108-38-3	C8H10	c(cccc1C)(c1)C	106.17	225.35	0.3618	0.5810	0.8604
118	PROPIONiC-anhydride	000123-62-6	C6H10O3	O=C(OC(=O)CC)CC	130.14	228.15	0.4639	0.8512	1.0057
119	Ethyl-acetoacetate	000141-97-9	C6H10O3	O=C(OCC)CC(=O)C	130.14	228.15	0.5466	1.1748	1.0227
120	Diethylene-glycol-diethyl-ether	000112-36-7	C8H18O3	O(CCOCC)CCOCC	162.23	228.15	0.6464	1.1773	0.9039
121	Ethynylbenzene	000536-74-3	C8H6	C(c(cccc1)c1)#C	102.14	228.35	0.4573	0.8012	0.9240
122	Mesitylene	000108-67-8	C9H12	c(cc(cc1C)C)(c1)C	120.19	228.45	0.3837	0.7064	0.8613
123	1-hexanol	000111-27-3	C6H14O	OCCCCCC	102.18	228.55	1.0206	3.6223	0.8159
124	Diacetone-alcohol	000123-42-2	C6H12O2	O=C(CC(O)(C)C)C	116.16	229.15	0.6458	2.1754	0.9342
125	1,2,4-trimethylbenzene	000095-63-6	C9H12	c(ccc(c1C)C)(c1)C	120.19	229.35	0.4377	0.8490	0.8722
126	1-heptanal	000111-71-7	C7H14O	O=CCCCCCC	114.19	229.85	0.5578	0.9051	0.8139
127	Diethyl-carbonate	000105-58-8	C5H10O3	O=C(OCC)OCC	118.13	230.15	0.4328	0.6547	0.9705
128	o-ethylaniline	000578-54-1	C8H11N	Nc(c(ccc1)CC)c1	121.18	230.15	0.9918	3.2562	0.9769
129	Di-n-hexyl-ether	000112-58-3	C12H26O	O(CCCCCC)CCCCCC	186.34	230.15	1.0578	2.4092	0.7896

130	p-diethylbenzene	000105-05-5	C10H14	c(ccc(c1)CC)(c1)CC	134.22	230.32	0.5161	0.9503	0.8580
131	Diisobutyl-ketone	000108-83-8	C9H18O	O=C(CC(C)C)CC(C)C	142.24	231.65	0.4853	0.8705	0.8017
132	Diethyl-phthalate	000084-66-2	C12H14O4	O=C(OCC)c(c(ccc1)C(=O)OCC)c1	222.24	232.65	1.4943	6.1012	1.1129
133	n-octyl-formate	000112-32-3	C9H18O2	O=COCCCCCCCC	158.24	234.05	0.6313	1.3048	0.8701
134	Diethylene-triamine	000111-40-0	C4H13N3	N(CCN)CCN	103.17	234.15	1.1708	3.3475	0.9545
135	N,N-diethylaniline	000091-66-7	C10H15N	N(c(cccc1)c1)(CC)CC	149.24	234.35	0.7060	1.5583	0.9306
136	n-octyl-acetate	000112-14-1	C10H20O2	O=C(OCCCCCCCC)C	172.27	234.65	0.7376	1.4847	0.8645
137	Anisole	000100-66-3	C7H8O	O(c(cccc1)c1)C	108.14	235.65	0.4576	0.8452	0.9906
138	n-octylbenzene	002189-60-8	C14H22	c(cccc1)(c1)CCCCCCCC	190.33	237.15	1.0743	3.1758	0.8528
139	2-heptanone	000110-43-0	C7H14O	O=C(CCCCC)C	114.19	238.15	0.4535	0.7777	0.8111
140	p-methylstyrene	000622-97-9	C9H10	c(ccc(c1)C=C)(c1)C	118.18	239.05	0.4224	0.7208	0.9156
141	1-heptanol	000111-70-6	C7H16O	OCCCCCCC	116.2	239.15	1.1489	4.4089	0.8195
142	n-pentanoic-ACID	000109-52-4	C5H10O2	O=C(O)CCCC	102.13	239.15	0.7805	1.6590	0.9331
143	Ethyl-benzoate	000093-89-0	C9H10O2	O=C(OCC)c(cccc1)c1	150.18	239.15	0.6867	1.4591	1.0424
144	3,3-diethylpentane	001067-20-5	C9H20	CCC(CC)(CC)CC	128.26	240.05	0.3042	0.4947	0.7500
145	4-heptanone	000123-19-3	C7H14O	O=C(CCC)CCC	114.19	240.15	0.3988	0.7166	0.8145
146	2-ethyl-butyric-acid	000088-09-5	C6H12O2	O=C(O)C(CC)CC	116.16	241.35	0.8889	2.1311	0.9194
147	2-octanol	000123-96-6	C8H18O	OC(CCCCCC)C	130.23	241.55	0.6506	4.2016	0.8171
148	o-diethylbenzene	000135-01-3	C10H14	CCc1ccccc1CC	134.22	241.95	0.4968	1.0328	0.8757
149	m-toluidine	000108-44-1	C7H9N	Nc(cccc1C)c1	107.16	241.95	0.4165	0.7645	0.8604
150	Styrene	000100-42-5	C8H8	c(cccc1)(c1)C=C	104.15	242.15	0.3754	0.6467	0.9004
151	1-methylnaphthalene	000090-12-0	C11H10	c(c(c(cc1)C)ccc2)(c2)c1	142.2	242.75	0.6946	1.4926	1.0164
152	2-heptanol	000543-49-7	C7H16O	OC(CCCCC)C	116.203	243.00	0.6840	3.2684	0.8141
153	Tetraethylenepentamine	000112-57-2	C8H23N5	N(CCNCCNCCN)CCN	189.3	243.15	12.5635	59.5677	0.9944
154	Decane	000124-18-5	C10H22	C(CCCCCCCC)C	142.28	243.45	0.5489	0.9881	0.7266
155	Phenetole	000103-73-1	C8H10O	O(c(cccc1)c1)CC	122.17	243.65	0.4956	0.9595	0.9605
156	Isovaleric-acid	000503-74-2	C5H10O2	O=C(O)CC(C)C	102.13	243.85	0.7327	1.6844	0.9263
157	trans-1-propenylbenzene	000873-66-5	C9H10	CC=Cc1ccccc1	118.18	243.85	0.3628	0.6323	0.9040
158	2-phenylethanol	000060-12-8	C8H10O	OCCc(cccc1)c1	122.17	246.15	0.8284	4.4280	1.0162
159	Benzaldehyde	000100-52-7	C7H6O	O=Cc(cccc1)c1	106.12	247.15	0.5834	1.0795	1.0415
160	Undecane	001120-21-4	C11H24	C(CCCCCCCCC)C	156.31	247.55	0.6335	1.2210	0.7365
161	1,2,3-trimethylbenzene	000526-73-8	C9H12	c(c(c(cc1)C)C)(c1)C	120.19	247.75	0.3936	0.8053	0.8909
162	o-xylene	000095-47-6	C8H10	c(c(ccc1)C)(c1)C	106.17	247.95	0.4204	0.7231	0.8764

163	n-nonylbenzene	001081-77-2	C15H24	c(cccc1)(c1)CCCCCCCCC	204.36	249.15	1.0965	2.4302	0.8522
164	Phenylacetonitrile	000140-29-4	C8H7N	N#CCc(cccc1)c1	117.15	249.35	0.6267	1.5035	1.0116
165	1,2,3,5-tetramethylbenzene	000527-53-7	C10H14	c(cc(c(c1C)C)C)(c1)C	134.22	249.45	0.4751	1.0684	0.8866
166	1-octanal	000124-13-0	C8H16O	O=CCCCCCCC	128.21	250.15	0.7280	1.1972	0.8180
167	n-hexylamine	000111-26-2	C6H15N	NCCCCCC	101.19	250.25	0.4237	0.8345	0.7607
168	n-butyl-benzoate	000136-60-7	C11H14O2	O=C(OCCCC)c(cccc1)c1	178.23	250.75	0.8325	4.4883	1.0007
169	Diethyl-succinate	000123-25-1	C8H14O4	O=C(OCC)CCC(=O)OCC	174.2	252.15	0.4929	1.6184	1.0356
170	Methyl-diethanolamine	000105-59-9	C5H13NO2	OCCN(CCO)C	119.16	252.15	4.7445	41.3376	1.0335
171	Dimethyl-maleate	000624-48-6	C4H8O4	O=C(OC)C=CC(=O)OC	144.13	254.15	1.0126	2.1889	1.1484
172	n-heptylamine	000111-68-2	C7H17N	NCCCCCCC	115.22	255.15	0.4916	1.0381	0.7717
173	1-nonanal	000124-19-6	C9H18O	O=CCCCCCCCC	142.24	255.15	0.8293	1.3917	0.8228
174	Methyl-decanoate	000110-42-9	C11H22O2	O=C(OC)CCCCCCCCC	186.29	255.15	0.7589	1.7276	0.8690
175	1,5-pentanediol	000111-29-5	C5H12O2	OCCCCCO	104.15	255.15	6.7880	52.5297	0.9891
176	1,1-diphenylethane	000612-00-0	C14H14	CC(c1ccccc1)c2ccccc2	182.27	255.25	1.1423	2.7552	0.9960
177	p-diisopropylbenzene	000100-18-5	C12H18	c(ccc(c1)C(C)C)(c1)C(C)C	162.27	256.15	0.4338	0.7728	0.8530
178	o-toluidine	000095-53-4	C7H9N	Nc(c(ccc1)C)c1	107.16	256.85	0.9009	2.5121	0.9945
179	2-ethyl-m-xylene	002870-04-4	C10H14	c(c(c(cc1)C)CC)(c1)C	134.22	256.95	0.4834	1.0441	0.8864
180	2-octanone	000111-13-7	C8H16O	O=C(CCCCCC)C	128.21	257.15	0.4738	0.9165	0.8146
181	1-octanol	000111-87-5	C8H18O	OCCCCCCCC	130.23	257.65	1.2893	5.4772	0.8230
182	Benzyl-alcohol	000100-51-6	C7H8O	OCc(cccc1)c1	108.14	257.95	1.0487	3.1837	1.0416
183	2-ethyl-1-butanol	000097-95-0	C6H14O	OCC(CC)CC	102.18	258.15	0.9379	4.1506	0.8289
184	Methyl-benzoate	000093-58-3	C8H8O2	O=C(OC)c(cccc1)c1	136.15	258.15	0.5452	1.2889	1.0846
185	Quinoline	000091-22-5	C9H7N	n(c(c(ccc1)cc2)c1)c2	129.16	258.37	0.8781	2.9129	1.0895
186	1-ethylnaphthalene	001127-76-0	C12H12	CCc1cccc2ccccc12	156.23	259.25	0.7314	1.6780	1.0042
187	Benzonitrile	000100-47-0	C7H5N	N#Cc(cccc1)c1	103.12	260.45	0.5532	1.0077	1.0008
188	o-nitrotoluene	000088-72-2	C7H7NO2	O=N(=O)c(c(ccc1)C)c1	137.14	263.15	0.6436	1.4588	1.1582
189	2,2,3,3-tetramethylpentane	007154-79-2	C9H20	CC(C)(C)C(C)(C)CC	128.26	263.35	0.3557	0.7865	0.7530
190	Dodecane	000112-40-3	C12H26	C(CCCCCCCCCC)C	170.33	263.55	0.7393	1.4954	0.7451
191	1-n-propylnaphthalene	002765-18-6	C13H14	c12c(CCC)cccc1cccc2	170.25	264.55	1.1087	2.9693	0.9868
192	Isophorone	000078-59-1	C9H14O	O=C(C=C(CC1(C)C)C)C1	138.21	265.05	0.7385	1.8822	0.9196
193	Methyl-salicylate	000119-36-8	C8H8O3	O=C(OC)c(c(O)ccc1)c1	152.15	265.15	0.3200	0.5175	0.8929
194	2-nonanone	000821-55-6	C9H18O	O=C(CCCCCCC)C	142.24	265.65	0.5491	1.1308	0.8176
195	n-heptanoic-acid	000111-14-8	C7H14O2	O=C(O)CCCCCC	130.19	265.65	1.2265	3.0676	0.9135

196	2-ethylnaphthalene	000939-27-5	C12H12	CCc1cc2ccccc2cc1	156.23	265.75	0.9342	2.1449	0.9889
197	Triethylene-glycol	000112-27-6	C6H14O4	O(CCOCCO)CCO	150.17	266.15	0.2805	0.4207	0.7245
198	1,2,3,4-tetramethylbenzene	000488-23-3	C10H14	c(c(c(c(c1)C)C)C)(c1)C	134.22	266.95	0.5468	1.3109	0.9004
199	2,6-dimethylpyridine	000108-48-5	C7H9N	n(c(ccc1)C)c1C	107.16	267.05	0.4275	0.7370	0.9177
200	5-nonanone	000502-56-7	C9H18O	O=C(CCCC)CCCC	142.24	267.25	0.5475	1.1246	0.8175
201	Tridecane	000629-50-5	C13H28	C(CCCCCCCCCCC)C	184.36	267.85	0.8529	1.7999	0.7536
202	1-nonanol	000143-08-8	C9H20O	OCCCCCCCCC	144.26	268.15	1.3868	6.7592	0.8247
203	1-decanal	000112-31-2	C10H20O	O=CCCCCCCCCC	156.27	268.15	0.9430	1.5879	0.8213
204	1-undecanal	000112-44-7	C11H22O	O=CCCCCCCCCCC	170.3	269.15	1.0576	1.7746	0.8233
205	n-hexanoic-acid	000142-62-1	C6H12O2	O=C(O)CCCCC	116.16	270.15	1.0117	2.3075	0.9201
206	Quinaldine	000091-63-4	C10H9N	n(c(c(ccc1)cc2)c1)c2C	143.19	271.65	0.6207	1.3739	1.0550
207	n-octylamine	000111-86-4	C8H19N	NCCCCCCCC	129.25	273.15	0.5757	1.2881	0.7790

Appendix E

List of publications

This appendix contains a list of journal publications including peer reviewed conference proceedings and a list of the conferences related to this PhD project. The results of this PhD work disseminated in form of a research article and 4 articles published as conference proceeding.

E. 1 Journal publications/peer reviewed conference proceeding.

1. **Yunus, N. A.**, Gernaey, K. V., Woodley, J. M., Gani, R. (2013). A systematic methodology for design of tailor-made blended products. Accepted to be published in Computers and Chemical Engineering. DOI number: 10.1016/j.compchemeng.2013.12.011.
2. **Yunus, N. A.**, Gernaey, K. V., Woodley, J. M., Gani, R. (2013). Design of sustainable blended products using an integrated methodology. *Computer Aided Chemical Engineering*, 32, 835-840.
3. **Yunus, N. A.**, Gernaey, K. V., Woodley, J. M., & Gani, R. (2012). Computer-aided approach for design of tailor-made blended products. In A. Aroussi, & F. Benyahia (Eds.), *Proceedings of the 3rd gas processing symposium* (pp. 303-310). Oxford: Elsevier.
4. **Yunus, N. A.**, Gernaey, K. V., Woodley, J. M., & Gani, R. (2012). An Integrated Methodology for Design of Tailor-Made Blended Products. *Computer Aided Chemical Engineering, 30,* 752-756.
5. **Yunus, N. A.**, Gernaey, K. V., Manan, Z. A., Woodley, J. M., & Gani, R. (2011). Design of tailor-made chemical blend using a decomposition-based computer-aided approach. *4th International Conference on Modeling, Simulation and Applied Optimization, ICMSAO 2011.*

E. 2 Conference contributions.

1. **Yunus, N. A.**, Hashim, H., Manan, Z. A., & Gani, R. (2010). "Design of feasible blends of gasoline and bio-fuels using a systematic computer-aided approach", Type: Oral, Presented at: PSE Asia, Singapore.
2. **Yunus, N. A.**, Gernaey, K. V., Woodley, J. M., & Gani, R. (2011). "Design of tailor-made fuels blends of gasoline and bio-fuels", Type: Poster, Presented at: International Congress on Sustainability Science and Engineering (ICOSSE'11), Arizona, USA.
3. **Yunus, N. A.**, Gernaey, K. V., Manan, Z. A., Woodley, J. M., & Gani, R. (2011). "Tailor-made design of chemical blends using decomposition-based computer-aided approach", Type: Oral, Presented at: International Conference on Modeling, Simulation and Applied Optimization (ICMSAO'11), Kuala Lumpur, Malaysia.
4. **Yunus, N. A.**, Gernaey, K. V., Woodley, J. M., & Gani, R. (2012). "Computer-aided approach for design of tailor-made blended", Type: Oral, Presented at: 3rd International Gas Processing Symposium, Doha, Qatar.
5. **Yunus, N. A.**, Gernaey, K. V., Woodley, J. M., & Gani, R. (2012). "An integrated methodology for design of tailor-made blended products", Type: Poster, Presented at: European Symposium on Computer Aided Process Engineering, (ESCAPE 22), London, UK.
6. **Yunus, N. A.**, Gernaey, K. V., Woodley, J. M., & Gani, R. (2012). "An integrated methodology for design of tailor-made blended products: Biofuels and bio-based lubricants", Type: Oral, Presented at: AIChE annual meeting, Pittsburgh, USA.
7. **Yunus, N. A.**, Gernaey, K. V., Woodley, J. M., & Gani, R. (2013). "Systematic design of tailor-made blended products", Type: Poster, Presented at: European Congress of Chemical Engineering, (ECCE), The Hague, The Netherlands.
8. **Yunus, N. A.**, Gernaey, K. V., Woodley, J. M., & Gani, R. (2013). "Design of sustainable blended products using an integrated methodology", Type: Oral, Presented at: European Symposium on Computer Aided Process Engineering, (ESCAPE 23), Lappenranta, Finland.

9. **Yunus, N. A.**, Gernaey, K. V., Woodley, J. M., & Gani, R. (2013). "Model-based blend design: Application to lubricant oils", Type: Oral, Presented at: PSE Asia, Kuala Lumpur, Malaysia.

NOMENCLATURE

Indexes

i	compound *i* in blend
j	compound *j* in blend
B	blend
k	target property
m	mixture

Notation

γ	activity coefficient
δ	solubility parameter ($MPa^{1/2}$)
ζ	target property
η	dynamic viscosity (cP)
ν	kinematic viscosity (cSt)
ν_0	kinematic viscosity of 0 VI oil at 40°C (cSt)
ν_B	kinematic viscosity of blend oil at 40°C (cSt)
ν_{100}	kinematic viscosity of 100 VI oil at 40°C (cSt)
ρ	density (g/cm^3)
ρ_a	amorphous density (g/cm^3)
ω	acentric factor
ΔH_c	heat of combustion (kJ/mol)

Nomenclature

ΔG^{mix}	energy of mixing
$[\eta]$	intrinsic viscosity
BI	blending index
C	cost
HHV	higher heating value (MJ/kg)
$-logLC_{50}$	lethal concentration (mol/L)
Mw	molecular weight (g/mol)
NC	number of compounds
P_c	critical pressure (bar)
P_{sat}	saturated vapor pressure (kPa)
PP	pour point (K)
R	gas constant
RON	research octane number
RVP	Reid vapor pressure (kPa)
SG	specific gravity
T_c	critical temperature
T_f	flash point (K)
T_m	melting point (K)
T_g	glass transition temperature (K)
T_r	reduced temperature (K)
V_{vap}	vapor loss (wt%)
VI	viscosity index
V_c	molar volume at critical point
Wt_{O2}	weight percent of oxygen (%)

$x_{1,LB}^{k,m}$	the lowest composition of component 1 in mixture, *m* that satisfies target property, *k*
$x_{1,UB}^{k,m}$	the highest composition of component 1 in mixture, *m* that satisfies target property, *k*
Z_{RA}	constant of the Modified Rackett equation

Abbreviations

2BE	2-butanone
2MT	2-methyltricosane
3ET	3-ethyltetracosane
3ME	3-methyleicosane
9ODA	9-octadecenoic acid
ACE	acetone
DFE	1H-dibenzo[a,i]fluorene, eicosahydro-
ETOH	ethanol
G	gasoline
GLY	propane-1,2,3-triol
MeTHF	furan, tetrahydro-2-methyl-
MO	mineral oil
MI	main ingredient
MoT	modeling tool
PE	polyethylene
THF	tetrahydrofuran
WCO	waste cooking oil

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